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IN ALL ITS APPLICATIONS TO

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SIR WILLIAM CROOKES, D.Sc., F.R.S., &c.

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THE CHEMICAL NEWS.

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No. 2510.—JANUARY 3, 1908.

LANDOLT'S EXPERIMENTS ON CHANGE OF WEIGHT IN CHEMICAL TRANSFORMATION.

By T. H. LABY.

Prof. Landolt has recently published (*Sitz. d. K. Akad. d. Wissen.*, 1906, viii., 266, and Chemical News, xciii. p. 271 *et seq.*) the results of his further experiments on this subject. It will be sufficient to quote the following passage to indicate his experimental methods :—"The substances were introduced separately into the two limbs of a glass vessel shaped thus ∩; the open ends of the vessel were then fused up, two such pieces of apparatus (A and B), of almost equal weight and of the same external volume, being prepared and placed upon the two scale pans of the balance. The difference of weight of these two vessels was then determined—(1) in the original condition, (2) after the reaction had taken place in apparatus A, (3) after the reaction had taken place in B, by which each experiment was performed twice."

The results of these new experiments, omitting many details, are shown in the Tables (see next page).

It is proposed to show (1) that in the "blank" and "solution" experiments the change in weight is equally often a gain as it is a loss of weight, and so is accidental; (2) the change in the reaction experiments, except in one case, is always a loss, and to some extent is proportional to the reacting mass.

Landolt has given in Table IV. the results obtained when the contents of the vessels undergo *no* chemical change, and such alterations of weight as were observed would consequently be due to the weighing error and change of weight of the vessel itself due to handling, &c. From a consideration of Landolt's methods the observation of a loss or gain in these experiments appears equally likely, and so in a number of experiments these will tend to balance. This is fully borne out by combining these results, thus :—

Blank Experiments (*Table* IV.).

8 + experiments : total gain, +0·067 mgrm. ; average, +0·008 mgrm.

11 − experiments : total loss, −0·107 mgrm. ; average, −0·01 mgrm.

19 + and − experiments : total change, −0·040 mgrm. ; average, −0·002 mgrm.

(A + experiment is one in which there is a gain of weight ; a − experiment one in which there is a loss).

As these results afford a standard of comparison it is most important to notice that the conditions of the experiments from which they were obtained were exactly similar to those of the reaction experiments, except that the heat of reaction of the latter was absent. For in Experiments 8 to 19 of Table IV. "the apparatus in which a reaction had already taken place was used, and the previous operation was repeated with the then homogeneous mass contained in it. To replace the missing heat of reaction in several experiments (4, 5, 10, 11), the vessel was placed for some time in an air-bath heated to 30—40°." In Table IV. it is seen that the observed changes in these experiments were :—Experiment 4, +0·002 mgrm. ; Experiment 5, −0·007 mgrm. ; Experiment 10, +0·015 mgrm. ; Experiment 11, −0·010 mgrm. ; or the average change was ± 0·000 mgrm. The importance of these four results will be referred to shortly.

Combining the solution experiments of Table IX. we get :—

Solution Experiments (*Table* IX.).

6 + experiments : with total gain +0·136 mgrm. ; average, +0·023 mgrm.

7 − experiments : with total loss −0·119 mgrm. ; average, −0·017 mgrm.

13 + and − experiments : with total change +0·017 mgrm. ; average, +0·001 mgrm.

Thus, under the conditions of Experiments IX. (a fall of temperature in 1 to 9 when AmCl dissolved in water)—conditions which are, excepting in the sign of the temperature change, exactly similar to the conditions of the reaction experiments of Tables V., VI., VII., VIII.—Landolt obtained + and − changes which balanced better than in the blank experiments of Table IV. Or in 32 (19+13) of his experiments the total losses and gains of weight were very nearly equal as seen in this table.

Blank and Solution Experiments Tables IV. *and* IX. *combined.*

14 + experiments : total gain, +0·203 mgrm. ; average, +0·014 mgrm.

18 − experiments : total loss, −0·226 mgrm. ; average, −0·012 mgrm.

32 + and − experiments : total change, −0·023 mgrm. ; average, −0·0007 mgrm.

In thirty-two experiments, then, there is a complete absence of a systematic error of one sign ; such errors as exist are of purely chance nature, and the losses and gains of weight equalise.

If there be no change of weight in the reaction experiments, cannot similar results to the above be expected for them ? The only want of similarity between the two is the absence in the blank and solution observations of the rise of temperature occurring in the reaction ones.

Blank Experiments (*Table* IV.).

No.	Contents of vessel.	Observed alteration of weight.
		Mgrm.
1.	Water	− 0·003
2.	,, ...	+ 0·005
3.	,, ...	+ 0·007
4.	,, ...	+ 0·002
5.	Paraffin oil	− 0·007
6.	Water	0·008
7.	Mercury	− 0·017
8.	I_2 and Na_2SO_4 solution ..	+ 0·014
9.	,, ,, ..	+ 0·012
10.	Cu and $FeSO_4$ solution ..	+ 0·015
11.	,, ,, ..	− 0·010
12.	,, ,, ..	− 0·023
13.	,, ,, ..	− 0·024
14.	Ag and $Fe_2(SO_4)_3$ solution ..	− 0·009
15.	,, ,, ..	+ 0·006
16.	,, ,, ..	− 0·002
17.	,, ,, ..	− 0·001
18.	$UO_2(NO_3)_2$ solution	+ 0·006
19.	,, ,, ...	− 0·003

Reaction Experiments (*Tables* V., VI., VII., VIII.).

No.	Cu, Ag, or I_2 separated.	Observed alteration of weight.
	Grms.	Mgrms.
Table V.: $Ag_2SO_4 + 2FeSO_4 = 2Ag + Fe_2(SO_4)_3$ or $AgNO_3$ + &c.		
4.	31·2	− 0·085
5.	24·2	− 0·103
6.	24·2	− 0·068
7.	24·2	− 0·042
8.	24·2	− 0·029
9.	63·5	− 0·199
10.	63·5	− 0·137
11.	63·5	− 0·079
12.	16·5	+ 0·003
13.	16·5	− 0·003
Table VI.: $Fe + CuSO_4 = Cu + FeSO_4$.		
1.	17·0	− 0·004
2.	17·0	− 0·022
3.	17·0	− 0·024
4.	17·0	− 0·041
Table VII.: $HIO_3 + 5HI = 6I + 3H_2O$.		
7.	43·3	− 0·120
8.	43·3	− 0·098
9.	64·9	− 0·004
10.	64·9	− 0·019
11.	64·9	− 0·033
12.	54·0	− 0·083
13.	54·0	− 0·053
Table VIII.: $2I + NaHSO_3 + H_2O = 2HI + NaHSO_4$.		
5.	50	− 0·021
6.	80	− 0·034

Solution Experiments (*Table* IX.).

No.	Salt.	Observed alteration of weight.
	Grms.	Mgrms.
1.	37·5	− 0·024
2.	37·5	− 0·002
3.	23·7	+ 0·008
4.	23·7	+ 0·005
5.	44·0	+ 0·078 ?
6.	44·0	+ 0·017
7.	60·0	− 0·008
8.	60·0	+ 0·019
9.	51·0	− 0·033
1.	72·5	− 0·038
1.	136·0	+ 0·009
2.	136·0	− 0·010
3.	136·0	− 0·004

The results, however, of the reaction experiments are quite unlike the ones so far considered. Thus:—

$Ag_2SO_4 + 2FeSO_4$ = &c. (*Table* V.).

1 + experiment: gain, + 0·003 mgrm.; average, + 0·003 mgrm.

9 − experiments: total loss, − 0·745 mgrm.; average, − 0·083 mgrm.

$Fe + CuSO_4$ = &c. (*Table* VI.).

4 − experiments: total loss, − 0·091 mgrm.; average, − 0·023 mgrm.

$HIO_3 + 5HI$ = &c. (*Table* VII.).

7 − experiments: total loss, − 0·410 mgrm.; average, − 0·059 mgrm.

$2I + NaHSO_3 + H_2O$ = &c. (*Table* VIII.).

2 − experiments: total loss, − 0·055 mgrm.; average, − 0·027 mgrm.

Tables V., VI., VII., VIII.

1 + experiment: gain, + 0·003 mgrm.; average, + 0·003 mgrm.

22 − experiments: loss, − 1·301 mgrms.; average, − 0·059 mgrm.

23 + and − experiments: change, − 1·298 mgrms.; average, − 0·056 mgrm.

How is it that the average change of weight in these "reaction" experiments, − 0·056 mgrm., is eighty times as great as in the "solution" and "blank" experiments, where it is − 0·0007 mgrm.? Only two kinds of explanations appear open to us, namely, (1) the vessels changed in weight to about the same extent as in the thirty-two "blank" and "solution" experiments (average, − 0·0007 mgrm.), and a loss of weight occurred in the weight of the reacting substances, which accounts for the observed change; (2) no loss of weight accompanied the chemical changes, but the heat of reaction caused the glass vessels to change in weight, and so the observed alteration arose. The whole question turns, then, on the effect of the heat of reaction on the weight of the vessels, Where Landolt heated the reaction vessels (blank Experiments 4, 5, 10, 11, Table IV,) to 30° or 40° C., as mentioned above, the total of the observed changes was ± 0·000 mgrm. Heydweiller also tried heating his vessels, and found "practically no alteration of weight could be proved." The little experimental evidence there is on the matter, then, is directly against a uniform loss of weight being caused by the rise of temperature due to the chemical reactions. And so explanation (2) would appear to fit the evidence better than (1).

The greatest difficulty, however, in accepting the observed alterations in weight of the reacting substances is (as Prof. Poynting indicated to me) the want of proportionality between the mass of the substances reacting and the observed change of weight. This is seen most in Experiments 9 and 11 of Table V., both in Thuringian glass:—(9) 63·5 grms. Ag separated, loss − 0·199 mgrm.; (11) 63·5 grms. Ag separated, loss − 0·079 mgrm.; while the total error of weighing, &c., if the same as that of the blank experiments, was not more than 0·015 mgrm. This want of proportionality is shown again in Experiments 7 and 9, Table VIII.

In the experiments of Table V., in which a silver salt was reduced to silver, the total silver separated in Experiments 4 to 13 was 351·5 grms. with a loss of weight of − 0·745 + 0·003 − 0·742 mgrm.; or, per 100 grms. of silver precipitated, of − 0·211 mgrm. This gives, assuming the loss of weight to be proportional to the Ag precipitated, the loss in each experiment in thousandths (0·001) of a mgrm., as shown under "calculated" in the table below. The results of the thirteen solution experiments (Table IX.) may be justly taken as showing that no change occurred in the weight of the contents of the vessel in those experiments, and such change as was observed was due, on this

view, to the errors of weighing, handling, &c. In the thirteen experiments, disregarding sign, the total observed change was 0·255 mgrm., or an average of 0·02 mgrm. The calculated losses are subject to this error of ± 20 thousandths of a mgrm.

Experiment.	Loss of weight.	
	Observed.	Calculated.
4.	−85	−65 ± 20
5.	−103	−51 ± 20
6.	−68	−51 ± 20
7.	−42	−51 ± 20
8.	−29	−51 ± 20
9.	−199	−134 ± 20
10.	−137	−134 ± 20
11.	−79	−134 ± 20
12.	+3	−35 ± 20
13.	−3	−35 ± 20

The want of proportionality in this reaction is not so great as it at first sight appears.

On the evidence of Landolt's experiments it may be said that it is probable that a loss of weight accompanies certain chemical reactions, and that the explanation which Landolt seems to favour of a loss through the walls of the vessel is supported by the irregularity in its amount.

THE DETERMINATION OF MANGANESE IN IN WATER.

By ROBERT SPURR WESTON.

The need for a convenient method of determining manganese in water has been recognised by many analysts. In the ordinary practice of the water analyst either the determination is made gravimetrically or it is omitted.

Manganese together with iron occurs in many ground waters, and very often its presence complicates or vitiates the processes used for the removal of iron from water supplies. At Breslau, in 1904, the sudden presence of manganese in the ground water made the supply useless for a time, notwithstanding the fact that the water was treated by aeration and filtration for the purpose of removing the iron from it.

Extremely valuable data are missing because of the inconveniences of the present time-consuming methods for the determination of manganese. Such data will be collected only if the methods be as facile as other methods used in water analysis. Waters rarely contain more than 10 milligrms. of manganese in a litre. Gravimetric methods are often beyond consideration, and the only ones which seem generally practicable are those in which the manganese is oxidised to permanganic acid. Of these latter the lead oxide methods of Chatard and others (Sutton's "Volumetric Analysis") and the sodium bismuthate method seemed to be the most promising. The sodium bismuthate method was used because of the greater ease with which the solution could be freed from the precipitate. This method has been used for the determination of manganese in ores and steels and is described by Blair (*Journ. Am. Chem. Soc.*, xxvi., 793). It was proposed by Schneider (*Dingler's Poly. Journ.*, cclxix., 224) and modified first by Reddrop and Ramage (*Journ. Chem. Soc.*, 1895, 268) and then by Brearley and Ibbotson ("The Analysis of Steel Works Materials").

The method is based upon the fact that in the presence of an excess of nitric acid a manganous salt is oxidised to permanganic acid by bismuth tetroxide. Blair states that:—

"The permanganic acid formed is very stable in nitric acid of 1·135 sp. gr. when the solution is cold, but in hot solutions the excess of bismuth tetroxide is rapidly decomposed, and then the nitric acid reacts with the permanganic acid, and as soon as a small amount of manganous salt is formed the remainder of the permanganic acid is decomposed, manganous nitrate dissolves, and manganese dioxide precipitates."

Reddrop and Ramage showed that it was difficult to get bismuth tetroxide free from chlorides, the presence of which would vitiate results, so they proposed the use of sodium bismuthate.

The manganese in the permanganic acid produced by oxidation may be determined in two ways. After filtering off the excess of bismuthate Blair adds an excess of ferrous sulphate to the filtrate, and by titration with permanganate solution determines the amount necessary to deoxidise the permanganic acid. For waters containing less than 1 mgrm. of manganese, however, comparison of the filtrate colorimetrically with permanganate run from a burette into an equal volume of dilute sulphuric acid free from organic matter contained in a Nessler tube, proved to be simpler and more precise; for larger quantities, however, the titration method should be used.

Method.

Evaporate with about 25 cc. of nitric acid (sp. gr. 1·135) enough of the sample of water to give from 0·01 to 1 mgrm. of manganese. Gently ignite the residue or bake it for half-an-hour at 130°. Add 50 cc. of nitric acid (sp. gr. 1·135) and when the solution is cool add about 0·5 grm. of sodium bismuthate. Heat until the pink colour disappears.

At this point Blair, in his determination of manganese in iron, adds sulphurous acid, ferrous sulphate, or sodium thiosulphate, to clear the solution if manganese dioxide is precipitated, and heats it to dispel all oxides of nitrogen. With waters this step was usually unnecessary, but whenever so, thiosulphate was the reagent used.

To the cool solution add sodium bismuthate in excess, stir a few minutes, and filter through thoroughly washed asbestos in a Gooch filter. Wash with dilute nitric acid, transfer filtrate to a large Nessler tube, and make up to 100 cc. with dilute nitric acid.

In another tube put 100 cc. of dilute sulphuric acid and add standard potassium permanganate solution until the colour of the sample is matched. The volume of potassium permanganate in cc. × 0·0001 gives the weight of manganese in grms. Express results as parts per million, —mgrms. per litre.

Reagents.

Potassium Permanganate Solution.—Dissolve 0·288 grm. of potassium permanganate in water and make up to 1 litre. 1 cc. is equivalent to 0·1 mgrm. manganese.

Nitric Acid (sp. gr. 1·135).—A mixture of three parts of water and one part of strong nitric acid (sp. gr. 1·42) is used.

Dilute Nitric Acid.—30 cc. of strong nitric acid to the litre.

Sulphuric Acid.—25 cc. of pure concentrated sulphuric acid to the litre. Add enough permanganate to colour the solution slightly but perceptibly pink.

Asbestos.—Prepare asbestos in the usual way by washing with acid and igniting. It should be free from organic matter.

Notes and Precautions.

The first experiments with this method gave unsatisfactory, erroneous results. Each reagent was tested to ascertain the cause of the error. It was found that the "C.P." nitric acid used was impure; it contained oxides of nitrogen. Several methods of purification were tried. The most efficient process proved to be that of passing a current of air through the concentrated acid for about half an-hour.

The presence of organic matter also vitiates results; when in large amounts the colour of permanganic acid does not appear in the filtrate. This difficulty is overcome by ignition of the residue or by baking it for half an-hour at 130°. The asbestos must be free from organic matter; otherwise the permanganic acid will be reduced.

The presence of chlorides also interferes with the determination. Samples which contain large amounts of chlorine should be treated before evaporation with a slight excess of silver nitrate and then filtered.

Experiments were made in which the bismuthate was added but once, the excess filtered off immediately, and the permanganic acid determined. Satisfactory results, however, were not obtained by this shorter method. The oxidation is complete only after the second addition of bismuthate.

The method is very delicate. It will detect 0·00002 grm. of manganese.

Experiments.

The first experiments were made with distilled water and known solutions of manganese sulphate and potassium permanganate. The results were as follows :—

No.	Manganese added. Grm.	Manganese recovered. Grm.
	A. *With Manganese Sulphate.*	
1.	0·00010	0·00009
2.	0·00010	0·00010
3.	0·00010	0·00010
4.	0·00050	0·00050
	B. *With Potassium Permanganate.*	
1.	0·00010	0·000095
2.	0·00020	0·00020
3.	0·00050	0·00045

C. Effect of Organic Matter.—Experiments were made like the above, except with the addition of varying volumes of leaf infusion, this being considered typical of the organic matter contained in water. The results were as follows :—

No.	Manganese added. Grm.	Leaf infusion. Cc.	Manganese recovered. Grm.
	(a) *Without Ignition of Residue.*		
1.	0·00010	1	0·00010
2.	0·00010	2	0·00008
3.	0·00010	10	0·00007
4.	0·00010	25	Colour faded in five minutes.
	(b) *Residue Ignited.*		
1.	0·00010	25	0·00010
2.	0·00010	25	0·00010

D.—Two trials of the method were made, first with Boston water, a surface supply, and second with Reading water, a ground water supply containing about two parts per million of iron. The Boston water contains no appreciable amount of manganese, but manganese is present in the Reading water. Besides determining the manganese in the water, determinations were made with the water containing varying amounts of added manganese.

No.	Taken. Cc.	Manganese added. Grm.	Manganese recovered. Grm.
	(a) *Boston Water.*		
1.	100	—	—
2.	100	0·00010	0·00009
3.	100	0·00010	0·00010
4.	1000	0·00010	0·00009
	(b) *Reading Water.*		
1.	100	—	0·000065
2.	100	—	0·000070
3.	100	—	0·000075
4.	100	0·00010	0·000170
5.	100	0·00010	0·000170
6.	100	0·00010	0·000165

E.—The following experiment shows the effect upon the determination of large amounts of chlorine.

No.	Boston City water. Cc.	Chlorine added to a litre. Mgrms.	Manganese added. Grm.	Manganese recovered. Grm.
1.	1000	50	0·00010	0·000085
2.	1000	500	0·00010	0·000075
3.	100	50	0·00010	0·000079
4.	100	500	0·00010	0·000080
5.	100 (*a*)	500	0·00010	0·000080

(*a*) Boston water contains about 2·5 parts of chlorine per million.

The writer finds this method rapid, convenient, serviceable, and reasonably accurate. He recommends it to other analysts with the hope that more data regarding the manganese content of ground waters may be placed on record.

He also wishes to thank his friend, Professor Henry Fay, for fundamental suggestions, and to acknowledge the services of his assistant, Miss Grace Ide Fairchild, who has made most of the determinations.—*Journal of the American Chemical Society*, xxix., No. 7.

STUDIES ON CHARCOAL AND LIQUID AIR.*

By Prof. Sir JAMES DEWAR, M.A., LL.D., D.Sc., F.R.S., Fullerian Professor of Chemistry, R.I.

THE object of the lecture was to demonstrate experimentally a few novel applications of liquid air observed in the course of laboratory experiments. Some of them may be said to take the character of lecture illustrations, while others deal with an extension of the scientific uses of charcoal at low temperatures, a subject which was first discussed in a Friday Evening Discourse delivered by the Professor in the year 1896.

Electrical Stimulation at Low Temperatures.

Bodies cooled to the temperature of liquid air have the surface film of water, which is more or less deposited on them, frozen exceptionally hard, and therefore not in a good condition for the dissipation of any electric charge that may be given to them. The result is that a substance like glass cooled in liquid air is exceedingly easily electrified by friction, and retains its charge for a long time. This property of glass was shown in the following manner :—

A glass tube shaped like a two-pronged fork was arranged so that a magnified image of it could be projected on a screen. (See Fig. 1). The prongs were

FIG. 1.

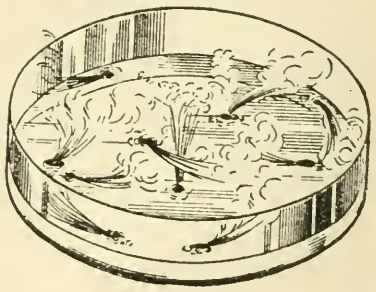


FIG. 2.

cooled in liquid air, and one prong, A, while it was being removed from the liquid air, was gently flicked with flannel

* A Discourse delivered at the Royal Institution, June 8, 1906.

or silk to electrify it. On being exposed to the air the moisture in the atmosphere was deposited as ice on both prongs, but the character of the deposit was different on the unelectrified and the electrified prong, crystals of ice beginning to form on the latter, speedily causing it to assume the appearance of a miniature forest of growing and moving crystals shown on A in Fig. 1, while B shows simply a dead coating of ice. The electrified prong by induction attracts the moisture in the air, and as fresh moisture is drawn in repulsion between like electricities causes the new crystals to be deposited as far out as possible, thus presenting the appearance in the diagram. With good projection one can see some of the crystals on A repelled and shot across to B. A similar experiment of another kind is the facility with which an electrified glass rod clears up ordinary opalescent liquid air by attaching the finely suspended impurities of ice crystals, solid carbonic acid, and organic matter to its surface when moved about in the liquid. The same thing may also be done by moving about a crystal of nitrate of uranium, which by cooling becomes highly electrified without the need of direct friction as when glass is used.

The Spheroidal State of Liquid Air on the Surface of Liquids.

As volatility depends on vapour pressure, of two liquids that having the higher vapour pressure at any given temperature is necessarily the more volatile. The difference in the facility of condensation of the vapours produced by different liquids may easily be demonstrated by the use of liquid air.

A series of liquids with different boiling-points, like tetrachloride of carbon, water, caustic potash solution, benzoic ether, and strong sulphuric acid, were selected, and each placed to the depth of about an inch in a number of shallow cylindrical cups, as shown in Fig. 2, the surfaces of which could in succession be projected on a screen by means of a horizontal lantern.

On allowing drops of liquid air to fall on the surfaces of these liquids, best by filtration through a small filter-paper funnel, they immediately assume the spheroidal state, and the projection through the liquid showed they were moving about with considerable rapidity, impinging on the sides of the vessel, and getting deflected like an elastic body, while followed by clouds of condensed vapour, the relative amount of which may be taken as roughly proportional to the volatility of the liquid. With water the cloud was very dense, being less so in the case of the alkali solution, more so for the tetrachloride of carbon, and least for sulphuric acid. On the sulphuric acid the drops moved about slowly owing to the high viscosity of the liquid, but with hardly any cloud, while on the surface of benzoic ester, a lively agitation accompanied by a light cloud was observed. In the case of the tetrachloride of carbon, the effect was most striking; dense clouds swayed to and fro over the surface, and the drops of liquid air shot to the walls of the vessel at all angles of incidence, and rebounded, followed by tails of vapour, making them look like miniature comets. In order to secure a good view of the movements, it is necessary occasionally to blow the fume away from the upper part of the vessel by a current of dry air. Care must be taken to avoid the fall of too much liquid air in one place, which would cause a rapid local cooling of the liquid attended with solidification, which inevitably arrests all spheroidal motion. This may be prevented to a great extent by having the liquids in the vessels used for projection slightly heated before the experiments are begun.

Thermal Conductivity.

Going to another subject, the well-known experiment of Ingenhousz on the relative conductivities of metals may be repeated at low temperatures by means of liquid air.

A vacuum-jacketed cup V (see Fig. 3) is filled with liquid air and covered with a sheet of mica (A B), having a set of small holes in it, through which a series of equal wires of different metals (copper, brass, bismuth, &c.) are fixed. After immersing their lower ends in the liquid air a coating of frozen moisture is deposited from the surrounding atmosphere, and is seen to collect round the lower parts of the wires above the mica screen, ultimately forming definite heights of an ice cap on each wire according to their conductivities. As in the Ingenhousz experiment, the relative conductivities are proportional to the squares of the heights to which the ice ultimately rises on the wires above the level of the mica sheet. In this manner it is possible to determine rapidly conductivities at low temperatures. The following table gives some rough measurements made in this way :—

	Height of ice in mm.	Conductivities (copper being taken as 1).
Bismuth	10	0·005
Fusible metal	27	0·035
Lead	38	0·069
German silver.. ..	40	0·076
Tin	54	0·139
Steel..	57	0·155
Iron	62	0·183
Brass	65	0·201
Copper	145	1·000

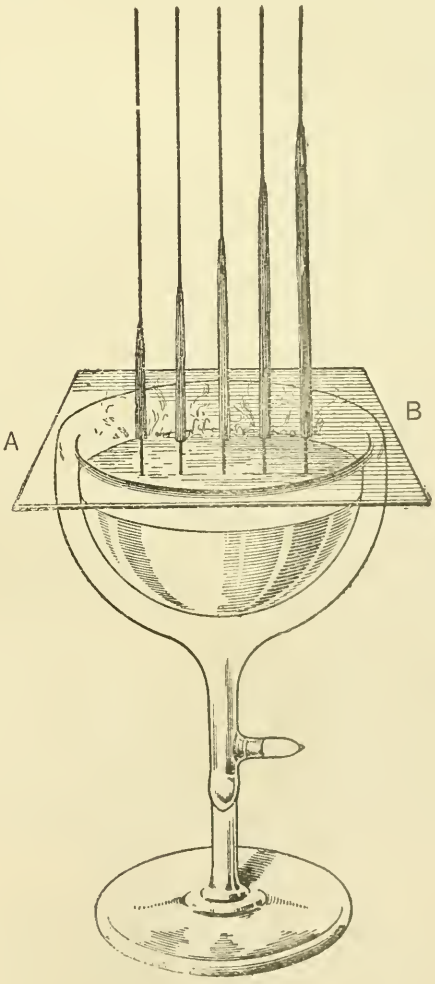


Fig. 3.

A similar method might be employed to determine conductivities at temperatures lower than the melting-point of

ice; for instance, the experiment might be made in a dry hydrogen atmosphere containing a small amount of sulphurous acid, continuously renewed, in which case the relative conductivities would be found from the melting-point of sulphurous acid instead of from that of ice.

Gas Absorption by Charcoal at Low Temperatures.

Some of the more important facts regarding the absorption of gases by charcoal at low temperatures were detailed in the Address given in 1905, entitled "New Low Temperature Phenomena," and to those a few additions were made due to further experience. Other porous materials are found to possess the power of absorption for gases at low temperatures to a less extent. Thus, dry aluminium oxide shows a remarkable power of absorbing air just like charcoal, 1 grm. condensing at atmospheric pressure some 70 cc., and the same property is possessed by meerschaum and silica. The retentive power of alumina is much inferior, however, to that of charcoal, and consequently is of no use in forming high vacua. All charcoals possess the property of gas absorption at low temperatures. Light charcoal, such as is used in the manufacture of gunpowder, or the variety got from animal substances like blood, both act, but experiments made at the Royal Institution show that charcoal prepared by careful carbonisation from cocoanut is one of the most convenient varieties to use. While using the same process of carbonisation, the absorptive effect is enhanced by making it take place slowly and with gradually increasing temperature. With the samples made a year ago, it was possible to get an absorption of about 150 cc. of air per grm. of charcoal at -185° C., but with care the amount can be raised to as much as 350 to 400 cc. per grm.

The amount absorbed at atmospheric pressure and at the temperature of liquid air can be quickly determined. A grm. of charcoal, previously heated to a red heat, is placed in a glass bulb connected by an indiarubber tube and stopcock to a graduated vessel containing air kept over strong sulphuric acid or a high boiling-point oil, so that on cooling the charcoal and opening the stopcock the absorption is measured. This absorptive power can be shown by means of the balance and the electro-magnet. From one arm of a balance was suspended a copper-wire gauze sphere containing charcoal which was carefully counterpoised. A flask partly filled with liquid air was now brought up below it, so that the vapour rising from the liquid air surrounded the charcoal. The absorption soon became visible through the beam of the balance descending as the charcoal became charged, and by adding weights the amount of gas absorbed per unit of time could be determined. If a rod of charcoal was hung up by a thread between the poles of an electro-magnet and sufficient torsion applied, so that its length was at right angles to the line joining the poles, when the magnetic field was produced, on bringing a vessel of liquid air close below it after a short time on turning on the electric current to "make" the magnet, the rod now set itself along the line joining the poles, proving that it had become magnetic. This action is dependent on the well-known magnetic property of oxygen, one of the constituents of the air, which surrounded the charcoal rod and which had condensed within its pores. On taking away the cool vapour of the liquid air the temperature soon rose, and the behaviour of the rod under magnetic action showed that it had lost the magnetic property.

Effect of Increased Pressure of Gas on the Absorption of Charcoal at Low Temperatures.

The absorption of hydrogen by charcoal at the temperature of liquid air and under atmospheric pressure is very considerable, and the question arises how much more could be got in by the use of higher pressure. The amounts absorbed by 6·7 grms. of charcoal, at the temperature -185° C. for various pressures, are given in the following table:—

Pressure in atmospheres.	Volume in cc.
1	620
5	925
10	1050
15	1000
20	975
25	925

The amount absorbed is seen to increase with the pressure to 10 atmospheres, after which the absorption in the pores of the charcoal seems to be independent of the pressure. At the temperature of liquid air this sample of charcoal would not absorb more than 1 litre of hydrogen, even when the pressure was raised from 10 to 25 atmospheres or the absorption had come to a limit. Increased absorption, which does not reach more than twice that at the ordinary atmospheric pressure, is the sole result of the use of higher pressures.

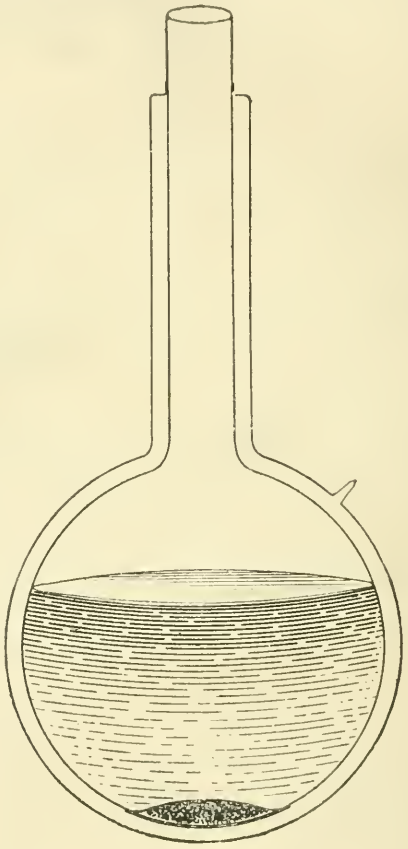


Fig. 4.

Vacua produced by Charcoal under different Circumstances.

The absortive power of charcoal for air is very remarkable. On stopping the passage of a stream of air into a charcoal bulb immersed in liquid air, to which a small manometer was attached, hardly any gas pressure was shown. This was further exemplified by the action of a Röntgen tube, partially exhausted, connected to a charcoal bulb. On immersing the bulb in liquid air the characteristic phosphorescent glow of the Röntgen tube was soon reached, but disappeared when the liquid air was removed. When hydrogen was used instead of liquid air, the pressure was so much reduced that the glow was entirely stopped. A Crookes's radiometer, filled with hydrogen at atmospheric pressure, had a charcoal bulb attached. On immersing the

charcoal bulb in liquid air no rotation took place, even when the beam of an electric lamp was thrown upon it; but when liquid hydrogen replaced the liquid air the motion became exceedingly rapid. This shows that high vacua can be attained by the use of charcoal in an atmosphere of pure hydrogen, provided it is cooled in a liquid hydrogen bath instead of liquid air. A similar radiometer, filled with helium at atmospheric pressure, remains inactive even when liquid hydrogen is the cooling agent, thus proving that the absorption of the helium by charcoal at 20° abs. is relatively inefficient for the production of vacua as compared with hydrogen. This is only another mode of proving the much greater volatility of helium over hydrogen.

Laws of Absorption at Low Temperatures.

The general laws of the dependence of the absorptive power of charcoal upon the pressure, temperature, and volume of the gas absorbed are apparently complicated, but in average circumstances they can be stated approximately. For a supply of gas at constant pressure the volume and temperature are related by a curve of hyperbolic form. There must clearly be a lower limit of temperature for absorption, for the gas will eventually liquefy; on the other hand, however small the absorption may be, as the temperature rises it can never entirely vanish. If the temperature be kept constant we should expect an increased absorption with increasing pressure up to a certain limit. Experiment indicates that this is the case, and we have again a curve of hyperbolic form connecting pressure and volume, but differing from the previous case in having the convexity turned the opposite way. When the pressure is small the absorption will be a minimum, but any slight increase of pressure will be associated with the molecular attraction of the charcoal, and the absorption may be expected to increase much more rapidly in proportion to the pressure. Finally, when the volume absorbed is kept constant the relation between the pressure and the temperature is of a logarithmic form, like those of a saturated vapour or a dissociating body.

For the absorption of hydrogen in charcoal at the temperature of liquid air the expression $\log p = a + bV - cV^2$ holds, where p is pressure, V the volume of gas occluded, and a, b, and c constants. For small concentrations of gas the pressure grows in a linear relation to the volume.

Hypothetical Densities of Gases Occluded in Charcoal.

Mitscherlich's measurements made on the charcoals used by him showed that in a piece of charcoal the space occupied by charcoal-substance is to the pore-space nearly in the ratio of 13 to 20. The Professor's observations on the real and apparent densities of cocoanut charcoal lead to the conclusion that in 100 grms. the pore-space may be taken on the average as about 15 cc. This enables us to compare the average hypothetical density of any absorbed gas with the density of the same gas when liquefied. The following table shows some such comparisons, and it may be noted that the densities of the absorbed gases at their boiling-points are equal to or a little greater than the corresponding liquefied gases at the same temperatures, so far as they are known. Whether the density of the monadic gases will turn out as satisfactory is a matter for future inquiry.

Gas.	Temperature of absorption. Cent.	Abs.	Density of gas occluded in charcoal.	Density of gas liquefied
Carbonic acid .	+15°	288°	0·7	0·8
Oxygen	−183°	90°	1·33	1·12
Nitrogen ..	−193°	80°	1·00	0·84
Elecrolytic gas	—	—	0·58	?
Hydrogen ..	−193°	80°	0·06	0·07
„ ..	−210°	63°	0·08	—
„ ..	−252°	21°	0·11	—
Helium	−258°	15°	0·17	?

Metallic Vacuum Vessels.

With the aid of charcoal, it is easy to make useful vacuum vessels of metal instead of glass. The metallic vessels resemble the ordinary glass silvered vessels, and are of from 2 to 10 litres capacity (see Fig. 4). The envelopes may be made of brass, copper, nickel, or tinned iron, with necks made of a bad conducting alloy. The vacuum between the walls of these vessels was maintained by enclosing some charcoal in a small globular space, A, constituting part of the inner vessel that is filled with liquid air. The necks may be covered with silvered glass vacuum cylinders which act as stoppers, and at the same time utilise the cold of the slowly evaporating liquid. The efficiency of the best metallic flasks is equal to that of the chemically silvered glass vacuum vessels, now generally used in low temperature investigation. Vessels of this type will be of use in industrial cryogenic operations and for the storage and safe transit of liquid air.

Diffusion of Gases into Charcoal at Low Temperatures.

Although, as regards general absorption, charcoal under corresponding conditions behaves in a similar manner to all gases, nevertheless it possesses a certain selective power, when in presence of a mixture of gases. A quantity of charcoal which has been heated, exhausted, and then saturated with ordinary air at −185° C., must have gases occluded in its pores of the average composition of the air. Let, however, a stream of air at the same low temperature pass slowly and continuously over it for some hours, and it will be found that at first the issuing gas is almost pure nitrogen, while the occluded gas reaches a new and definite composition. If now the gas absorbed by the charcoal be expelled by heating it to the ordinary temperature, it will contain on the average some 60 per cent of oxygen. Fig. 5

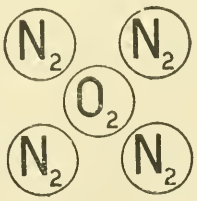


Fig. 5.

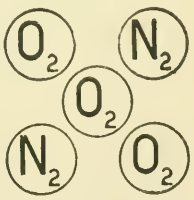


Fig. 6.

represents roughly the molecular composition of the air initially present in the pores of the charcoal, namely, about four molecules of nitrogen to one of oxygen. The final average molecular composition of the absorbed gas after the passing of the slow current of air, cooled to −185° C., over the charcoal is similarly represented in Fig. 6, where it can be seen that diffusion, or fractional distillation at constant temperature, has gone on until about two of the molecules of nitrogen have been replaced by two of oxygen. If the charcoal, in equilibrium with air gases in the condition specified in Fig. 6, has a current of hydrogen at the temperature of liquid air passed over it, the hydrogen will diffuse in, until about one molecule in five is present, as shown in Fig. 7. Again, if charcoal be

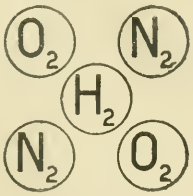


Fig. 7.

saturated with oxygen to begin with, and hydrogen be passed over it when cooled to −185° C., the hydrogen will

diffuse in, until it constitutes one-third of the gas present in the pores (Figs. 8 and 9). Similarly, if we employ

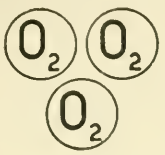


Fig. 8.

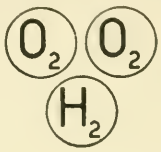


Fig. 9.

nitrogen in place of oxygen, the hydrogen will displace about two-thirds of the nitrogen (Figs. 10 and 11). On the

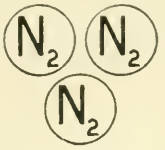


Fig. 10.

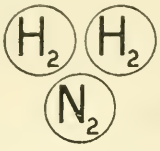


Fig. 11.

other hand, if the charcoal be initially saturated with hydrogen at -185° C. (Fig. 12), and air passed over it at that temperature, the whole of the hydrogen is practically displaced, and the gas remaining in the charcoal is represented by the composition shown in Fig. 13, which is the same as in Fig. 6.

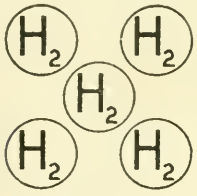


Fig. 12.

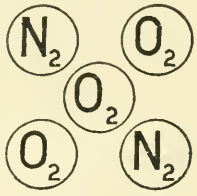


Fig. 13.

If, instead of analysing the whole of the occluded gas that is given off, samples are taken from the charcoal between definite temperatures, from the boiling-point of air up to the ordinary temperature, then a regular fractionation of the occluded gases takes place, resembling that of an ordinary mixed liquid, and the problem is an entirely different one. Further, even in the simpler mode of treatment as described above, the relative proportions of the absorbed gases depends at any time after the experiment has started upon the relation between the current of gas used at the constant temperature of -185° C. and the nature and condition of the charcoal. The simplification of the problem is due to making the time very long.

(To be continued).

Metacetaldehyde.—A. Hantzsch and J. Oechslin.—By determining the molecular weight of both freshly prepared and old specimens of pure metacetaldehyde, the authors have shown that this compound exists in only one form. It is quite stable when pure, and dissolves in phenol solutions without undergoing any change. It is not trimolecular in phenol solution, but undoubtedly tetramolecular, $(C_2H_4O)_4$; and in thymol solution it is most probably hexamolecular, $(C_2H_4O)_6$. It is undoubtedly not an isomer of paraldehyde, but a polymer of higher molecular weight. As its molecular weight varies from $(C_2H_4O)_6$ to $(C_2H_4O)_4$, according to the phenol used as solvent, it is probable that in the solid state it is a high polymer of diacetaldehyde, $(C_2H_4O)_{2n}$, which depolymerises more or less according to the nature of the medium. This agrees with the fact that metaldehyde is much more easily totally depolymerised than paraldehyde. —*Berichte*, xl., No. 15.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 19th, 1907.

Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

The President referred to the death of Lord Kelvin, and stated that the Society would be represented at his funeral.

It was also announced that the Society had lost through death Mr. Samuel Hall, and Prof. B. J. Harrington, of McGill University, Montreal.

Messrs. P. V. Dupré, G. H. Martin, C. P. Matthews, W. S. Mills, M. Wechsler, E. Wheeler, and R. Whymper were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Guy Barr, B.A., B.Sc., 79, Fillebrook Road, Leytonstone, N.E.; Walter Brown, jun., Brookvale, Strathaven, N.B.; David Cowan Crichton, M.A., B.Sc., A.I.C., Backhill House, Musselburgh; Andrew L. Scott, F.I.C., Fir Lodge, Cheshunt, Herts; John Armstrong Smythe, 15, The Poplars, Gosforth, Newcastle-on-Tyne; Charles Sedgley Spiers, The Woodlands, Scalford Road, Melton Mowbray; John Watson, B.Sc., 5, Kendrew Street, Darlington; William Henry Withey, B.A., Stroud, Glos.; Joseph Yates, 18, Park Street, Haslingden, Lancs.

Certificates have been authorised by the Council under By-law I. (3) in favour of the following:—Puran Singh, Dehra Dun, India; Archibald Edgar Collens, Government Laboratory, Port of Spain, Trinidad.

Of the following papers, those marked * were read:—

*254. "*Attempted Synthesis of* β—N—β / β—CHβ *-Dinaphthacridine; Condensation of Methylene Dichloride and* 1-*Substituted*-2-*naphthylamines.*" By Alfred Senier and Percy Corlett Austin.

In attempting to synthesise derivatives of the unknown β—N—β / β—CHβ -dinaphthacridine (compare Senier and Austin, *Trans.*, 1906, lxxxix., 1387) by condensing methylene dichloride with derivatives of β-naphthylamine in which the hydrogen of the α-position adjacent to the amino-group had been substituted, the authors have found that when the substituent was a halogen, either Reed's dinaphthacridine or a meso-derivative thereof was formed, thus completing the proof that this base has the constitution assigned to it. In the case of 1-nitro-2-naphthylamine, no acridine was obtained.

1-Chloro-2-naphthylamine reacts with methylene dichloride to form β—N—β / α—CHα -dinaphthacridine. 1-Bromo-2-naphthylamine and methylene dichloride yield *7-bromo-*β—N—β / α—CHα *-dinaphthacridine*, which crystallises from benzene in yellow needles, melting at 215·5° (corr.). Its solutions are fluorescent, and it differs from the halides of the dinaphthacridines (Senier and Austin, *Trans.*, 1904, lxxxv., 1196), as it may be boiled with potassium hydroxide solution, and even distilled under reduced pressure, without decomposition.

The *hydrochloride*, *aurichloride*, and *platinichloride* are yellow powders.

With glacial acetic acid, the base forms a deep yellow crystalline *compound*, melting at 273°. Reduction with stannous chloride leads to the production of bis-β—N—β / α—CHα dinaphthacridine dihydride.

*255. "*Cobaltamine Compounds.*" (Preliminary Note). By Charles Edward Groves.

During the past few years, the author has investigated some of the cobaltamine compounds, and owing to the recent appearance of papers on the subject, he considers it advisable to publish a preliminary account of some of the results obtained.

Crimson Carbonate.—When freshly-precipitated cobalt carbonate, suspended in dilute ammonia, is agitated with air and then exposed to the air for three or four days, the solution becomes brownish red, and deposits bright crimson crystals. These can be purified by recrystallisation from water at about 45°, or, better, from a very dilute solution of ammonium bicarbonate. The carbonate is readily decomposed by acids with evolution of carbon dioxide, and formation of the corresponding salts. It is almost insoluble in cold water, but on heating gently (45°) the crystals dissolve; at a higher temperature, the solution becomes brown and turbid. The substance is practically insoluble in dilute ammonia in the cold, and very little dissolves even on heating. It is almost insoluble in dilute alcohol even on boiling. The author purposes, provisionally, calling this compound *carycinocobaltamine carbonate* (καρύκινος, blood-red).

Blue-black Compound.—This is formed when the crimson carbonate is treated with nitro-hydrochloric acid. On gradually adding the latter to the carbonate under water, it dissolves with effervescence, but on adding more of the acid a red crystalline precipitate is produced, which if left in the liquid for a day or more is converted into the "bluish black" crystals. This compound dissolves readily in concentrated ammonia, forming a rose-coloured liquid. When boiled with hydrochloric acid, it is, apparently, completely converted into the purpureo chloride. In an aqueous solution of ammonium bicarbonate, it dissolves to a purple liquid.

Bronze-green Chloride and the corresponding *Nitrate.*—Of these two salts, the nitrate is the more readily prepared, and it can be easily converted into the chloride, which is bronze-green, the colour of the nitrate being greyish-green. The nitrate is most easily prepared by gradually adding a solution of cobalt nitrate in dilute nitric acid, in the proper proportion, to a mixture of dilute ammonia with a solution of ammonium persulphate contained in a large flask, and, after it is thoroughly oxidised by shaking it with air, acidifying the mixture with dilute nitric acid.

This nitrate is almost insoluble in water, but dilute ammonia dissolves it readily, forming a pink solution, and it is also soluble in ammonium bicarbonate solution. It is neither altered nor dissolved by nitric acid, whether concentrated or dilute, and it is also insoluble in boiling acetic acid, but on adding concentrated hydrochloric acid to the mixture it dissolves at once.

The hydrochloride is easily obtained from the nitrate by heating the latter with dilute hydrochloric acid (1 : 2) at 70° for twenty to twenty-five minutes. It can easily be recrystallised from hot very dilute hydrochloric acid, when it separates in long, bronze-green needles. The purified hydrochloride dissolves in cold water, forming a deep blue liquid, but this soon decomposes, especially when warmed, depositing a brown powder, apparently cobaltous-cobaltic oxide.

Grass-green Compound.—If purpureo-cobaltic chloride (or nitrate) is heated for some hours with dilute ammonia, or, better, ammonium carbonate solution, it dissolves, and the dark red solution containing roseo-cobaltic salt, if kept for some time, deposits a crystalline mass consisting of minute pink needles. After these have been separated, concentrated nitric acid is added to the mother-liquor, the brick-red precipitate thus formed is removed by filtration, and a slow current of crude nitrosyl chloride passed into the purple-red filtrate. This after twenty-four hours deposits a mixture of red and green crystals. These can be separated by washing with water, which easily dissolves the red crystals, leaving the grass-green compound, which is comparatively insoluble in water.

This green salt is only sparingly soluble in water and in dilute ammonium bicarbonate solution, and is practically insoluble in alcohol and dilute acids. When boiled with dilute hydrochloric acid, it appears to be converted into the purpureo-chloride.

*256. "*The Direct Interaction of Aryl Halides and Magnesium.*" By James Frederick Spencer and Eleanor Marguerite Stokes.

The authors find that cyclic halogen compounds react with magnesium powder without the use of ether when the two substances are heated together. The products, which are of the type R·MgX, are light grey solids, and are readily decomposed by water with considerable evolution of heat and production of the hydrocarbon: $R{\cdot}MgI + H_2O = R{\cdot}H{\cdot} + Mg(OH)I$.

Iodo- and bromo-benzene yielded benzene and diphenyl; *p*-iodo- and *o*-bromo-toluene gave toluene; *m*-bromo- and *o*-chloro-aniline gave aniline; *p*-bromo-phenol yielded phenol, and α-bromonaphthalene and bromoacenaphthene gave the respective hydrocarbons. The yields in all these cases were extremely good. Chloro-substitution products do not react generally in this way. In the case of aliphatic compounds, methyl iodide, methylene iodide, and *iso*propyl iodide were indifferent, but bromosuccinic acid gave succinic acid.

Discussion.

Dr. McKenzie pointed out the interest of the observations of the authors in connection with Tschelinzeff's results with the "individual" magnesium compounds of the type R·MgX, obtained by the interaction of magnesium and halogen compounds in benzene solution with the use of dimethylaniline as catalyst.

In view of the results of Schroeter (*Ber.*, 1903, xxxvi., 3005) on the action of carbon dioxide on magnesium phenyl bromide, Dr. McKenzie asked if the formation either of triphenylcarbinol or benzophenone had been noted by the authors in the experiment on the formation of benzoic acid described by them.

Dr. Spencer replied that, owing to the large yields obtained, triphenylcarbinol and benzophenone had not been looked for, and their formation could only take place to a small extent, if at all.

257. "*Derivatives of Tetramethyl Glucose.*" By James Colquhoun Irvine and Agnes Marion Moodie.

Tetramethyl glucoseoxime, which was obtained as a mixture of α- and β-forms melting at 61—68°, shows in methyl-alcoholic solution a specific rotation of +25·9° without mutarotation. The constitution of the compound, deduced from its behaviour on alkylation and the hydrolysis of the product, shows that it does not possess the normal oxime structure, but is produced by the reaction of the sugar in its γ-oxidic forms. Similar arguments point to the fact that tetramethyl glucoseanilide also possesses the γ-oxidic linking, and is not derived from an alkyloxyaldehyde. The compound melted at 132—134°, and gave $[\alpha]_D^{20}$ +229·5° in acetone solution.

Tetramethyl chloroglucose and *tetramethyl bromoglucose* were obtained as uncrystallisable syrups, which, in their reactions, closely resemble the corresponding tetra-acetyl compounds. As they were readily converted into a mixture of α- and β-tetramethyl methylglucosides when treated with methyl alcohol and silver oxide, the preparations doubtless consisted of mixtures of α- and β-forms.

Negative results were obtained in attempts to produce acetal derivatives of tetramethyl glucose, and the application of the Grignard reaction also led to no result.

With one doubtful exception, all the derivatives studied indicate that the alkylated sugar reacts invariably in the γ-oxidic form, but this characteristic linking appears to be absent in tetramethyl glucose-hydrazone.

In the course of the work, it was found that the silver oxide method of alkylation can be readily applied to the methylation of different types of oximes, thus furnishing a convenient method of determining the hydroxyl content of such compounds.

258. "*The Characterisation of Mercerised Cotton.*" (Preliminary Note). By Julius Hübner.

The author has studied the action of a number of reagents on cotton, both before and after mercerisation, and finds that the following methods afford a certain means of distinguishing between mercerised and non-mercerised cotton, and also enable the degree of mercerisation to be approximately ascertained.

The cotton to be examined is steeped in a saturated solution of potassium iodide containing iodine; after a few seconds' immersion, the sample is withdrawn and washed five or six times in a 2 per cent potassium iodide solution. After this treatment, mercerised cotton is found to have acquired a brownish-black colour, whilst unmercerised cotton remains white; on then treating the samples with water, the mercerised cotton turns bluish-black and the unmercerised sample remains quite white.

Another convenient method for distinguishing between mercerised and untreated cotton consists in steeping the samples in an aqueous solution, 100 cc. of which contain 93·3 grms. of zinc chloride and about 0·005 grm. of iodine; in this liquid, non-mercerised cotton remains practically white, whilst the mercerised material becomes of a dark navy-blue colour.

259. "*Note on the Action of Metallic Calcium on Alcohols.*" By Frederick Mollwo Perkin and Lionel Pratt.

It has been stated that metallic calcium has no action on alcohol, and may therefore be employed as a dehydrating agent for alcohols. The authors find, however, that, when metallic calcium is allowed to remain in contact with ethyl or methyl alcohol for from thirty to sixty minutes, reaction ensues and may become very vigorous. Once started the reaction continues to completion, according to the equation $2CH_3.OH + Ca = (CH_3{\cdot}O)_2Ca + H_2$.

If the mixture is heated to the boiling point of the alcohol, the reaction proceeds much more rapidly. With propyl, *iso*butyl, amyl, and benzyl alcohols, the reaction takes place exceedingly slowly at the ordinary temperature, but completes itself in the course of a few hours at the boiling point of the alcohol. Analysis shows the white, amorphous powder obtained in all cases to be $(Alk{\cdot}O)_2Ca$.

260. "*Note on the Iodates and Periodates of the Alkalis and the Ammonium Radicle.*" By Thomas Vipond Barker.

The author gave a description of rubidium periodate, together with an account of some specific gravity and solubility determinations of the iodates of rubidium and cæsium, and the periodates of sodium, potassium, rubidium, cæsium, and ammonium.

261. "*The Colour of Cupric Salts in Aqueous Solution.*" By Nevil Vincent Sidgwick and Henry Thomas Tizard.

The authors have measured the depth of colour of aqueous solutions of cupric salts from the point where they become blue, and the influence on it of the anion and the concentration, using the Donnan tintometer. The main results are:—

1. All the salts examined (propionate, acetate, formate, monochloroacetate, chloride, bromide, sulphate, nitrate) showed the same tint at dilutions greater than about N/4, but the depth of colour varied with the anion and the dilution. This shows that they contain at least two substances of the same tint, but of different depths of colour.

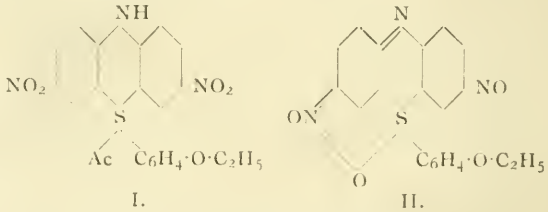
2. The weak acid salts are deeply coloured at high concentrations, and the more so the weaker the acid. On dilution, the colour diminishes, tending to a value from two to four times that for copper sulphate, according to the acid, and hence greater than that of the cupric ion. It is therefore suggested that the change is due to the dissociation of CuA_2 into $CuA^{\cdot}$, which must then proceed very far before the second dissociation giving $Cu^{\cdot\cdot}$ ions begins. The second dissociation constant of a ternary salt, MX_2, should be very small, in accordance with Ostwald's theory for dibasic organic acids, as the positive charge on the metal in the ion $MX^{\cdot}$ will resist the appearance of a second charge on M.

3. The salts of strong acids are always much paler than those of weak. On dilution the colour deepens, but only slightly. With copper nitrate, the complexes formed in very concentrated solution are of the same blue colour as the copper ion, but deeper.

4. It thus seems probable that ionisation affects the intensity of the colour, but not the tint.

262. "*Derivatives of S-Phenylphenazothionium.*" (Part I.). By Samuel Smiles and Thomas Percy Hilditch.

The α- and β-dinitro-compounds obtained from thiodiphenylamine by the action of nitric acid (Bernthsen, *Annalen*, 1885, ccxxx., 116) yield the sulphates of bases when condensed with phenetole in presence of concentrated sulphuric acid. Thus Bernthsen's view that these substances are sulphoxides is confirmed. The condensation products referred to are salts of S-phenetyl-3:3′-dinitrophenazothionium (I.); these are converted by aqueous alkali into the reddish brown fluorescent thetine (II.). Hydrolysis of the salts furnishes the crimson sulphonium hydroxide. Derivatives of S-phenetyl-N-methylphenazothionium have been prepared in the same way; here, as with the above-mentioned compounds, the salts are green, but the base is dull brown and not fluorescent. A synthesis of these substances was attempted by the condensation of di-*p*-nitrodiphenylamine and phenetole-*p*-sulphinic acid, but the reaction could not be carried beyond the intermediate stage of the sulphoxide.



I. II.

263. "*A Colorimetric Method for the Determination of Small Percentages of Iron in Copper Alloys.*" By Arnold William Gregory.

The method is based upon the colour reaction given by salicylic acid and ferric chloride. This reaction is modified by using a solution of salicylic acid in acetic acid, and the test is carried out in the presence of sodium acetate. Under these conditions, a deep red colour is produced, which is used as a colorimetric test for iron in small quantities. The interfering action of the blue copper salts is overcome by the addition of a weak solution of potassium cyanide, which results in the formation of the colourless complex cyanide of copper and potassium.

Zinc and antimony do not interfere with the reaction, but lead must be removed as sulphate.

This method has been found to give very accurate results in cases where the percentage of iron in the copper alloys is so low that the ordinary gravimetric methods of estimation involve the use of a large quantity of the alloy.

264. "*The Effect of Heat on the Alkyl Iodides.*" By Zelda Kahan.

Experiments an the effect of heating alkyl iodides alone and in the presence of zinc, sodium, silver chloride, and barium peroxide show that the probable course of the reaction is:—

1. The dissociation of the alkyl iodide into hydrogen iodide and an alkylene or alkylidene derivative.

2. If alkylidene is formed, its conversion into an ethylene derivative.

3. The reduction of the ethylene derivative by the hydrogen iodide. When heated alone, ethyl iodide yields ethane, ethylene, and a little hydrogen, but in the presence

of zinc, butane is also formed in amount proportional to the quantity of zinc employed. Methyl iodide decomposes much less readily than any of the alkyl iodides, yielding chiefly methane and ethylene; with zinc, ethane is also formed, but with barium peroxide the chief products are carbon mono- and di-oxides and methane.

The normal and *iso*propyl iodides, when heated alone, yield only propane, but with zinc or sodium much propylene and some hydrogen are also formed.

265. "*The Influence of Acids and Alkalis on the Velocity of Formation of Acetoxime.*" By Ernest Barrett and Arthur Lapworth.

At 0° and at a dilution of 1 grm.-molecule each of acetone and hydroxylamine per 40 litres, the velocity of oxime formation is least with no other base or acid present. The acceleration caused by sodium hydroxide is very large and nearly proportional to the concentration of that substance. The acceleration caused by hydrochloric acid is also considerable, and rises rapidly until when half a grm.-molecule of acid is present the velocity is more than fifty times as great as at first. With more acid, a very rapid fall occurs, and attains a nearly constant velocity when rather more than 1 grm.-molecule of acid is present.

With acetaldehyde, very similar results were obtained.

The measurements were carried out before the appearance of Acree and Johnson's recent paper (*Journ. Am. Chem. Soc.*, 1907, xxxviii.. 258).

266. "*Action of Metallic Calcium on Ketones.*" By Herbert Drake Law and Frederick Mollwo Perkin.

When metallic calcium is placed in contact with acetone which has previously been dried over calcium chloride, a slow evolution of hydrogen takes place, which becomes brisker in the course of a few hours. The rate of evolution of gas is about 2 litres in twenty-four hours at an average temperature of 16°. If the calcium and acetone are allowed to remain in contact for about one week and the product then fractionated, about 200 to 300 grms. of mesityl oxide are obtained from 2 litres of acetone. More complex substances are also formed in considerable amount. If the acetone remaining after fractionation is again placed in contact with the same quantity of calcium, a further yield of mesityl oxide is obtained. The proportions for which the best results have been obtained are about 150 grms. of metallic calcium and 2 litres of acetone. After standing for four days, 200 to 300 grms. of mesityl oxide are obtained. When acetone is heated with metallic calcium, it is difficult to stop the reaction at the right point to obtain mesityl oxide, and products of high boiling-point are formed.

Methyl ethyl ketone reacts very much more slowly with calcium, and the substances require to be left in contact for several months. When 1500 cc. of methyl ethyl ketone are allowed to remain in contact with 200 grms. of calcium for about one week, the rate of evolution of hydrogen is about 1 litre in twenty-four hours. On fractionation, at the end of eight to ten weeks, a considerable quantity of a fraction boiling at 164—165° is obtained, and also a larger quantity of fractions boiling up to 300°. The lower fraction is probably *γ-methyl-Δγ-heptene-ε-one*, $CH_3{\cdot}CH_2{\cdot}C(CH_3){:}CH{\cdot}CO{\cdot}CH_2{\cdot}CH_3$.

On oxidation with potassium permanganate, acetic acid and methyl ethyl ketone are obtained. This does not actually prove the correctness of the formula just given, because the same results would be obtained by oxidation of the compound $CH_3{\cdot}CH_2{\cdot}C(CH_3){:}C(CH_3){\cdot}CO{\cdot}CH_3$.

The substance is a colourless liquid, having a very fragrant odour resembling that of oil of bergamot.

267. "*The So-called 'Tetrabromodiphenoquinone' and the Constitution of Coerulignone.*" By James Moir.

The author has continued his researches on Magatti's tetrabromodiphenoquinone (*Proc.*, 1906, xxii., 110), and has studied the action of reducing agents on this compound.

268. "*A Note on Certain Pyrogenic Reactions.*" By Norman Thomas Mortimer Wilsmore and Alfred Walter Stewart.

In the course of some investigations on the effect of a white-hot platinum wire on various organic substances, the authors have made the following observations. The apparatus employed was in essentials the same as the generator used in the case of keten (*Trans.*, 1907, xci., 1938). The results obtained were qualitative only, no analysis being made.

Owing to its possible use as a solvent, the behaviour of benzene was investigated; it was not affected by the wire, and toluene also was unacted on.

When ethyl crotonate is treated pyrogenically, ethylene is liberated, and crotonic acid crystallises from the cooled liquid which remains in the generator. An unsaturated acid, namely, cinnamic, was then tried in benzene solution, but no effect was observed. On the other hand, when saturated ethereal salts were placed in the generator, a mixture of carbon dioxide and hydrocarbons was liberated. The decomposition, in the case of ethyl acetate, appears to take place in the following steps:—

$$CH_3{\cdot}CO_2{\cdot}C_2H_5 \rightarrow CH_3{\cdot}CO_2H + C_2H_4 \rightarrow$$
$$\rightarrow CH_4 + CO_2 + C_2H_4.$$

In the case of ethyl malonate, ethylene is first evolved, as in the foregoing case, and the malonic acid thus formed breaks down into carbon dioxide and acetic acid, which, in its turn, decomposes into methane and carbon dioxide. It is to be noted that whenever any acetyl derivative is formed in the course of any of these stages, some keten is in turn produced from it. In contradistinction to the behaviour of the fatty acids, benzoic acid in benzene solution was not noticeably attacked.

From these results, the authors conclude that the ethylenic linking in the *α*-position with respect to the carboxyl group tends to render the compound more stable with regard to this agent than is an ethane derivative. This view is, of course, supported by the fact that unsaturated hydrocarbons are more stable in the electric arc than saturated ones.

From acetone, keten was obtained, whilst substances of high boiling point, such as anethole and aniline, were decomposed with charring.

FARADAY SOCIETY.

Ordinary Meeting, December 17th, 1907.

Dr. F. Mollwo Perkin, Treasurer, in the Chair.

Dr. F. G. Donnan, in the absence of the author, read a paper on "*A Physico-chemical Study of the Complex Copper Glycocoll Sulphates*," by J. T. Barker, B.Sc. (Will be inserted in full).

Dr. F. Mollwo Perkin read a paper on "*The Discovery of the Alkali Metals by Davy: the Bearing of the Discovery upon Industry.*" (The lecture was illustrated with lantern slides).

After a short biographical sketch the author refers to Davy's early experiments on galvanism, which began in 1800, and culminated in 1807 in the electrolytic decomposition of the fused alkalis, caustic soda, and caustic potash, described on November 19th in the Bakerian Lecture before the Royal Society, entitled "On some New Phenomena of Chemical Changes produced by Electricity, particularly the Decomposition of the Fixed Alkalis, and the Exhibition of the New Substances which constitute their Bases, and on the General Nature of Alkaline Bodies." Davy's experiments are described in detail, and it is shown that the E.M.F. of his battery must have been about 220 volts, and the current he used something under 1 ampère. The subsequent experiments on the decomposition of the alkaline earths, by which calcium, strontium, barium, and magnesium in the form of amalgams were obtained, are then described.

The second part of the paper deals, among other matters, with the industrial manufacture by Wohler in

1827 of potassium, by Ste. Claire Deville in 1854 of sodium, with Watt's suggestions (1851) for electrolysing fused sodium chloride, with Castner's chemical sodium process (1886), and his electrolytic process (1890), Rathenau and Suter's sodium process, Becker's process, and the process of Darling, who electrolysed fused sodium nitrate, using porous partitions.

NOTICES OF BOOKS.

Photographisces Hilfsbuch ("Photographic Guide"). Part II. By HANS SCHMIDT. Berlin: Gustav Schmidt. 1907.

THIS book is meant for the serious worker who is willing to give both time and trouble to the preparation of good photographs, and who will not be satisfied with turning out anything but first-class work. Beginners will find it very helpful, more especially as comparatively little is left to the worker's judgment, and nearly always explicit statements and definite rules of working are given. At the same time experienced photographers will no doubt learn something from its perusal. The second volume treats only of the production of the print from the negative. Firstly, processes are described which should be applied to unsatisfactory negatives in order to improve them before printing from them, and the sorting and touching up of negatives are carefully discussed. The value of the different printing papers in use is estimated, and details of printing, toning, and fixing are then given. Various methods of mounting and similar practical questions are also dealt with, and while the book is very full and clear the author avoids verbosity, and shows himself to be an excellent judge of what are the essential points which the uninitiated want constantly emphasised in order that they may get satisfactory results.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Society of Chemical Industry, 8. "Preparation of Paratoluidine from Mixed Toluidines by means of Paratoluidine Hydrate," by R. J. Friswell. "The Determination of Small Quantities of Bismuth," by H. W. Rowell.

TUESDAY, 7th. } Royal Institution, 3. (Christmas Lectures, adapted
THURSDAY, 9th. } to a Juvenile Auditory). "Astronomy, Old and New," by Sir David Gill, K.C.B., F.R.S., &c.

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THE CHEMICAL NEWS.

Vol. XCVII., No. 2511.

THE VOLUMETRIC ESTIMATION OF TIN BY MEANS OF POTASSIUM DICHROMATE.

By H. REYNOLDS, B.Sc., Ph.D.

"The method, originally devised by Streng, for the direct estimation of tin by potassium dichromate or other oxidising agents in acid solution has been found most unsatisfactory from the fact that variable quantities of water or acid seriously interfere with the accuracy of the results. The cause is not fully understood, but that it is owing partly to the oxygen mechanically contained in the water reacting on the very sensitive stannous chloride there can be very little doubt, as the variations are considerably lessened by the use of water recently boiled and cooled in closed vessels." (Sutton, "Volumetric Analysis," 9th Edition, p. 345).

The two points to be considered in the estimation of Sn by means of $K_2Cr_2O_7$ are:—

1. The prevention of oxidation during solution and titration.
2. The determination of the end-point.

1. Streng's method (*Pogg. Ann.*, 1854, xcii., p. 57) of dissolving the metal in boiling HCl and pouring the solution into a beaker for titration could not give exact results. The greatest care is necessary to prevent oxidation, especially if the solution is heated.

The following analyses illustrate this point, the column headed "Difference" giving a measure of the amount of oxidation which took place:—

	Taken.	Found.	Difference.	Per cent.
a.	0·1469	0·1413	0·0056	96·27
b.	0·1417	0·1376	0·0041	97·08
c.	0·1498	0·1253	0·0245	83·6
d.	0·1317	0·1285	0·0032	97·58

Remarks.

a. The metal was dissolved in a boiling tube fitted with a Bunsen valve; after the addition of 22 cc. $K_2Cr_2O_7$, the contents of the tube were transferred to a conical flask owing to the inconvenience of titrating in the tube. The total amount of $K_2Cr_2O_7$ required was 23·75 cc.

b. The gauze basket was removed before titrating, and washed down with a few cc. cold distilled water.

c. The basket was washed with about 20 cc. of warm water on withdrawing it from the flask.

d. The basket was left in until 21 cc. $K_2Cr_2O_7$ had been added (total amount required, 21·60).

In all the analyses the granulated metal was placed in a platinum gauze basket about 1 cm. diameter and 1 cm. deep, which was lowered into 5 cc. concentrated HCl. In the last three analyses a small flask fitted with a Bunsen valve was used instead of the boiling tube.

Fourteen more analyses were carried out in this way, 10 cc. concentrated HCl being used in each case. The solution was made at about 30° C., and when it was complete, or nearly so, the contents of the flask were heated until a brisk evolution of HCl took place, and allowed to cool to the temperature of the room before the flask was opened for the titration. N/10 $K_2Cr_2O_7$ was used for all these analyses, of which the extreme cases are shown below.

Taken.	Found.	Difference.	Per cent.	Remarks.
0·1539	0·1492	0·0047	96·96	Smallest amount of tin taken.
0·2385	0·2339	0·0046	98·07	Largest amount of tin taken.
0·1930	0·1889	0·0041	97·87	Smallest difference.
0·2250	0·2190	0·0060	97·32	Largest difference.

Mean difference, 0·0049

At this point a change was made in the method, the Bunsen valve being no longer used, and instead a current of CO_2 was passed through the conical flask from before the introduction of the metal until the greater part of the $K_2Cr_2O_7$ had been run in. The gas was not passed into the solution but delivered just above it. It escaped through a tube wide at the top and narrow below, with a side hole just below the cork. When the solution was ready for titration the $K_2Cr_2O_7$ was run in through this tube to within about 1 cc. of the correct amount. The necessary quantity of indicator was then added through the same tube, and followed by two or three drops of water. The titration was finished in the open flask, more CO_2 being passed in if necessary.

Five analyses were carried out under these conditions, the quantity of tin taken varying from 0·1974 grm. to 0·2110 grm., and the difference from 0·0018 to 0·0026, with a mean difference of 0·0022 grm. These analyses were all of granulated tin supplied by Merck, and it probably contained about 99·5 per cent Sn. Assuming this, the mean oxidation, using the Bunsen valve, would be 0·0039 grm., and using the CO_2, 0·0012 grm.

Six analyses were made with Kahlbaum tin in the same way; the amount of metal taken varied between 0·1412 grm. and 0·2302, and the difference between the quantity taken and that found varied from 0·0007 to 0·0023 grm., the mean value being 0·0016. For these analyses a weaker solution was used than for those with Merck tin, viz., 1 cc. = 0·0200 grm. Sn, instead of N/10; the volume of solution required is thus greater in the ratio of 6 to 5, and this may account for the slightly greater oxidation which took place.

It thus appears that, if certain precautions be taken, the deficit due to oxidation need not exceed about 0·001 grm. of Sn. This amount can be made unimportant by increasing the amount of tin used for each analysis to about a grm. The precautions to be observed are that the metal shall be dissolved in an atmosphere of CO_2, and that the solution shall be kept in this atmosphere until the titration is almost finished.

2. The determination of the end-point, by observing the colour change caused by the presence of unchanged $K_2Cr_2O_7$, is not practicable with any degree of accuracy. In place of it Streng suggested adding a few drops of KI starch solution to the solution to be titrated. Other available indicators are $FeSO_4$ with KCNS and indigo-carmine. With regard to the latter, the change from the green of the chromic solution to the blue of the indigo-carmine is not always a very easy one to observe; as to the former, it is perhaps doubtful if the KCNS would remain unaffected in the strongly acid reducing solution.

If azobenzene is heated with concentrated H_2SO_4 until the beginning of a violent reaction, and the whole is then poured into a large volume of water, a deep red solution is obtained, containing possibly an oxyazobenzene sulphonic acid. This is reduced to a colourless body by $SnCl_2$, and $K_2Cr_2O_7$ then added restores the colour. If the solution is made alkaline it goes almost magenta coloured, and shows a brick-red fluorescence. The colour is very intense, and the substance is thus a very suitable indicator for use with bichromate when oxidising strong reducing agents. For the red colour to mask the Cr green completely, when oxidising 1 grm. of tin, about 3 cc. of indicator are necessary of a strength = 0·034 cc. of a $K_2Cr_2O_7$ solution, of which 1 cc. = 0·01 grm. Sn. A solution of ferrous sulphate, or of Mohr salt, does not affect the indicator, nor does $Na_2S_2O_3$. It is thus not available for the titration of

weak reducing agents; this has the advantage that a strong reducer like $SnCl_2$ can be estimated in presence of a weak one like $FeCl_2$.

In all the titrations with $K_2Cr_2O_7$ in this work the azo-benzene derivative was used as indicator. In addition the end-point in the ferro-tin analyses was checked by taking out a drop and testing with KCNS.

The general details of the method having been thus settled, analyses were made of pure tin from Kahlbaum, ferro-tin, and Britannia metal with satisfactory results as follows :—

I. *Kahlbaum Tin.*

A. 0·8316 grm. tin was weighed out in the platinum gauze basket, and dissolved in 15 cc. concentrated HCl in a current of CO_2. When solution was complete 41 cc. $K_2Cr_2O_7$ were run in through the short tube, the indicator added, and the titration finished in artificial light.

41·54 cc. $K_2Cr_2O_7$ were required = 0·8308 grm. Sn = 99·90 per cent.

The chromic solution was red in certain lights before the indicator was added, but by reflecting a strong light from a sheet of white paper through a layer 0·5 cm. thick it was quite green. The solution was distinctly green after 41·50 cc. had been run in.

B. 0·7392 grm. tin dissolved in 14 cc. HCl as above, 36 cc. $K_2Cr_2O_7$ added, and then the indicator. The titration was finished in artificial light.

Required, 36·90 cc. = 0·7380 grm. Sn = 99·84 per cent.

For the following analyses the CO_2 was obtained from a cylinder of the gas, and the HCl for the analysis was heated almost to boiling in the flask in an atmosphere of CO_2 to expel any air it might contain. When the acid had cooled, the gauze basket containing the metal was lowered into it.

C. 0·7331 grm. tin was dissolved in 20 cc. HCl, the solution being warmed three or four times during the process. 72·5 cc. $K_2Cr_2O_7$ (1 cc. = 0·01 grm. Sn) were run in, followed by 3·2 cc. indicator. The titration was finished in good daylight, the end reaction being very sharp.

Required, 73·22 cc. = 0·7322 grm. Sn = 99·88 per cent.

D. 0·6383 grm. tin was dissolved in 20 cc. HCl. Solution took about half-an-hour. At the last the acid was heated almost to boiling to dissolve a few remaining specks of tin.

After leaving five minutes to cool, 63·1 cc. $K_2Cr_2O_7$ were run in, and 3 cc. indicator added. The titration was finished in good daylight, the end reaction being very sharp.

Required, 63·77 cc. = 0·6377 grm. Sn = 99·91 per cent.

For this last analysis the CO_2 was passed through a titanous sulphate solution before entering the flask.

Two gravimetric analyses were made by dissolving the metal in HNO_3 and converting into SnO_2.

	I.	II.
Metal taken ..	0·5049	0·4195
SnO_2 found ..	0·6408	0·5321
Sn	= 0·5050 = 100·02 %	= 0·4194 = 99·98 %

Results.

	Volumetric.	Gravimetric.
A.	99·90	I. 100·02
B.	99·84	II. 99·98
C.	99·88	—
D.	99·91	—
Mean ..	99·88	100·00

The method has therefore no serious inherent faults, and the precautions taken against oxidation are not at all complicated or difficult to carry out.

The case of pure tin being thus satisfactorily disposed of, I proceeded to see how far the method was applicable to tin alloys. Ferro tin, manganese tin, phosphor tin, pewter, and Britannia metal have been investigated, and of these manganese tin, pewter, and phosphor tin have so far not yielded good results. The manganese tin gave a very indistinct end reaction, the indicator taking a dirty brown colour on oxidation instead of returning to its original crimson-red, although an aqueous solution of pure $SnCl_2$ and $MnCl_2$ gave a beautiful end reaction. The phosphor tin gave very discordant results, the phosphorus in one instance appearing to take part in the reaction. In this case 0·702 grm. alloy required 82·2 cc. $K_2Cr_2O_7$, corresponding fairly closely to 95 per cent Sn, being oxidised from $SnCl_2$ to $SnCl_4$, and 5 per cent P being oxidised from P_2O_3 to P_2O_5. The end reaction in all cases was slow and was not always distinct.

II. *Ferro-tin.*

A. 0·8451 grm. of the alloy was weighed out in the platinum gauze basket, and dissolved in 20 cc. concentrated HCl, which had been previously heated and cooled in an atmosphere of CO_2. The whole analysis was as usual carried out in the same atmosphere. A slight black flocculent residue remained undissolved, and probably consisted of a trace of C. 77·9 cc. $K_2Cr_2O_7$ were run in through the tube, followed by 3 cc. indicator.

Required, 79·30 cc. = 0·7930 grm. Sn = 93·84 per cent.

B. 0·7359 grm. of the alloy was dissolved as usual, leaving a slight black residue. 68 cc. $K_2Cr_2O_7$ were run in, followed by 3 cc. indicator.

At 68·90 Solution greenish red; no permanent colour with KCNS.
,, 68·95 Green tinge in solution; slight colour with KCNS.
,, 69·00 No green visible in solution; red colour distinct and permanent with KCNS.

Half a drop more made no difference in the appearance of the solution nor in the coloration with KCNS, when a drop was taken out and tested on a tile.

Required, 69·00 cc. = 0·6900 grm. Sn = 93·76 per cent.

C. 0·7043 grm. of the alloy was dissolved as usual. Solution was not quite complete, there being a slight residue of C even after boiling. 63·5 cc. $K_2Cr_2O_7$ were added at once, followed by 3 cc. indicator. At 66·00 cc. the solution was still greenish, and KCNS gave no permanent colour with a drop taken out. At 66·07 there was no green in the solution, and the red with KCNS was permanent.

Required, 66·07 cc. = 0·6607 grm. Sn = 93·81 per cent.

The titration was finished in good daylight.

It will be seen from B and C that the return of the colour of the indicator coincides with the appearance of the colour with the KCNS; that is to say, that the oxidation of the $SnCl_2$ is complete before that of the $FeCl_2$ begins. At the same time, the end reaction is slower than with pure tin, the cause being evidently that—

$$SnCl_2 + Cl_2 = SnCl_4$$

is not the only reaction, the pair of reactions—

$$FeCl_2 + Cl = FeCl_3$$
$$2FeCl_3 + SnCl_2 = SnCl_4 + FeCl_2$$

going on simultaneously with it towards the end of the titration.

D. 0·8158 grm. of the alloy was dissolved as usual. There was the usual slight presumably carbonaceous residue. 76·3 cc. $K_2Cr_2O_7$ were run, followed by 3 cc. indicator. The light was too bad for the colour of the solution to be seen clearly. At 76·54 a drop taken out gave a faint permanent red with KCNS, fainter than, but quite as permanent as, the coloration at 66·07 in C.

Required, 76·54 cc. = 0·7654 grm. Sn = 93·82 per cent.

The CO_2 for the last two analyses and for all the following ones was passed through a Wetzel washing-

bottle containing titanous sulphate before it entered the Erlenmeyer flask.

The control analyses were made volumetrically with iodine and starch in acid solution (*cf.*, S. W. Young, *Journ. Am. Chem. Soc.*, xix., 809), the method of dissolving being exactly as above. The strength of the iodine solution was such that 1 cc. = 0·01904 grm. Sn. It was checked against a N/10 $K_2Cr_2O_7$ solution by means of $Na_2S_2O_3$. The results obtained were :—

Grm.		Cc.		Grm.		Per cent.
1. 0·7362 alloy	required	36·30	I =	0·6911	Sn =	93·88
2. 0·6556	,,	32·35	,,	0·6159	,,	93·96
3. 0·7451	,,	36·72	,,	0·6991	,,	93·84

Results.

	By $K_2Cr_2O_7$.	By iodine.
A.	93·84	1. 93·88
B.	93·76	2. 93·96
C.	93·81	3. 93·84
D.	93·82	—
Mean ..	93·81	93·89

The second iodine estimation had to be finished off in a hurry, and there might have been a few tenths of a milligrm. of metal undissolved when the titration was begun.

III. *Britannia Metal.*

A. 0·6264 grm. of the alloy was dissolved in 20 cc. conc. HCl which had been heated previously in CO_2. A good deal of heating was necessary, and solution was not quite complete, a slight flocculent black residue remaining. 25 cc. $K_2Cr_2O_7$ were run in, and then 3·5 cc. indicator were added. The end reaction was rather slower than with pure tin, but much better than with ferro-tin. The end-point was sharp.

Required, 31·60 cc. = 0·3160 grm. Sn. = 50·45 per cent.

B. 0·6473 grm. was dissolved in 20 cc. conc. HCl which had not been previously heated. The contents of the flask were left cold until the greater part of the metal had dissolved; they were then heated to boiling at frequent intervals until no more gas was given off. 32 cc. $K_2Cr_2O_7$ were run in, followed by 3 cc. indicator.

Required, 32·75 cc. = 0·3275 grm. Sn = 50·55 per cent.

End reaction good, not too slow. End-point sharp. Colour brownish instead of bright crimson.

C. 0·9156 grm. was dissolved as above. 45·5 cc. $K_2Cr_2O_7$ were run in, followed by 3 cc. indicator.

Required, 46·40 cc. = 0·4640 grm. Sn = 50·68 per cent.

In B and C after the indicator had been added, the solution was heated almost to boiling in the current of CO_2 to re-dissolve the $PbCl_2$ precipitated on diluting with the $K_2Cr_2O_7$ solution. The titrations being finished hot the end reaction was fairly fast. The end-point in both cases was sharp.

D. 0·7581 grm. dissolved as above. 37·9 cc. $K_2Cr_2O_7$ were run in, followed by 3 cc. indicator. The solution was heated to re-dissolve $PbCl_2$. The end reaction was fast and sharp, the restored colour brownish.

Required, 38·50 cc. $K_2Cr_2O_7$ = 0·3850 grm. Sn = 50·78 per cent.

E. 0·8509 grm. dissolved as above. 42·5 cc. $K_2Cr_2O_7$ were run in, then 3 cc. indicator. The colour at the end was dirty brown, but on the addition of 1 cc. indicator the red was clear.

Required, 43·02 cc. = 0·4302 grm. Sn = 50·56 per cent.

F. 0·8166 grm. dissolved as above. 41·0 cc. $K_2Cr_2O_7$ run in, followed by 4 cc. indicator, and the solution heated to re-dissolve $PbCl_2$. The end reaction was very good, the colour changed from slightly dirty green to clear red with 0·02 cc.

Required, 41·40 cc. = 0·4140 grm. Sn = 50·70 per cent.

The control analyses were made exactly as in the case of ferro-tin with the following results :—

Grms.		Cc.		Grm.		Per cent.
1. 0·9318 alloy	required	24·78	I =	0·4718	Sn	50·63
2. 1·0077	,,	26·77	,,	0·5097	,,	50·58
3. 1·0765	,,	28·54	,,	0·5412	,,	50·55

Results.

	By $K_2Cr_2O_7$.	By iodine.
A.	50·45	1. 50·63
B.	50·55	2. 50·58
C.	50·68	3. 50·55
D.	50·78	—
E.	50·56	—
F.	50·70	—
Mean ..	50·62	50·59

Summary of Numerical Results.

	Control.	Found.	Diff. (per cent).
Pure tin	100·00	99·88	+0·12
Ferro-tin	93·89	93·81	+0·08
Britannia metal	50·59	50·62	−0·03

Summary.

A method has been worked out for the accurate estimation of tin by titration with $K_2Cr_2O_7$.

A sulphonation product of azobenzene was used as indicator, the colour change being from green to red. Kahlbaum tin, which by gravimetric analysis contained 100·00 per cent Sn, gave by this method 99·88 per cent. Ferro-tin and Britannia metal also gave good results.

The Method.

Place 20 cc. concentrated HCl in a 200 cc. Erlenmeyer flask, fitted with a cork, having a long and a short tube passing through it. The long tube should reach to about 1·5 cm. of the bottom of the flask; the short tube should be about 6 mm. wide at the top and 2 mm. at the bottom, which should be cut slantwise. The tube should also have a side hole just below the cork to allow the gas to escape while the $K_2Cr_2O_7$ is running in. Fill the flask with CO_2 from a cylinder, the gas passing first through titanous sulphate to free it from oxygen, and then through a little H_2SO_4 to free it from titanous sulphate. Heat the HCl nearly to boiling, and allow to cool in the current of CO_2. Weigh out 0·6 to 1·0 grm. of the metal in a platinum gauze basket, and lower into the acid. When no more gas is evolved heat nearly to boiling to drive any dissolved hydrogen out of the solution, cool down and run in $K_2Cr_2O_7$ through the short tube to within about 1 cc. of the correct amount. Add indicator in sufficient quantity to be sure that the green colour of the chromic salt will be entirely masked when the colour of the indicator is restored. Remove the basket, and finish by delivering the remainder of the $K_2Cr_2O_7$ direct into the solution.

The Chemical Laboratory,
L.C.C. Paddington Technical Institute,
December, 1907.

Royal Institution.—On Tuesday next, Jan. 14, at 3 o'clock, Dr. A. A. Gray delivers the first of two lectures at the Royal Institution, on "The Internal Ear of Different Animals"; and on Thursday, Jan. 16, Prof. W. W. Watts will deliver the first of two lectures on (1) "The Building of Britain." On Saturday, Jan. 18, Prof. Gisbert Kapp commences a course of two lectures on "The Electrification of Railways." The Friday Evening Discourse on Jan. 17 will be delivered by Prof. T. E. Thorpe, on "The Centenary of Davy's Discovery of the Metals of the Alkalis"; and on Jan. 24 by Colonel David Bruce, on "The Extinction of Malta Fever."

STUDIES ON CHARCOAL AND LIQUID AIR.*

By Prof. Sir JAMES DEWAR, M.A., LL.D., D.Sc., F.R.S., Fullerian Professor of Chemistry, R.I.

(Concluded from p. 8).

Chemical Interactions in High Vacua.

If a piece of pure sulphur (S) is put in one end and some mercury (Hg) in the other end of a U-tube (Fig. 14), both substances being kept at the temperature of liquid air during the time required to reach a high vacuum by the mercurial pump or by charcoal exhaustion, and the whole sealed off and left to stand at the ordinary temperature; then in a few hours, it will be noted that the surface of the mercury which was at first a brilliant reflecting one gets tarnished from the formation of a film of sulphide of mercury. The mercury vapour pressure being much greater than that of sulphur, it would be expected that any formation of sulphide of mercury taking place would be seen on the sulphur side of the U-tube. But the contrary

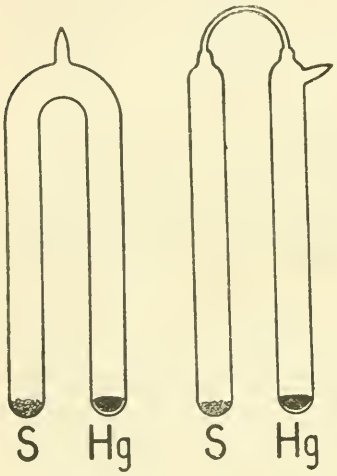


Fig. 14.

Fig. 15.

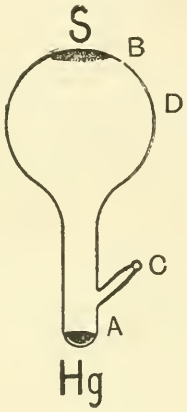


Fig. 17.

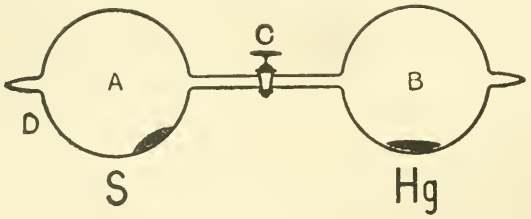


Fig. 16.

is the case, as the sulphide is seen to form at first on the surface of the mercury (Hg). The explanation that suggests itself is that the ordinary molecule of sulphur containing 6 to 8 atoms, dissociates and throws off single or double atoms which make their way rapidly through the mercury vapour without wholly combining with it, until they reach the surface of the liquid mercury, when the conditions for chemical interaction are more favourable. If the tube be constricted as at M (Fig. 15), the activity of the sulphur atoms on the mercury surface is stopped, as they encounter the mercury atoms under the most favourable circumstances for combination in the narrow tube at M, and there form the sulphide which is quite visible after long keeping.

It is interesting to note the excessively small quantities of the respective elements that are interacting in this case. The pressure of mercury vapour at 15° C. is about $1\frac{1}{2}$ millionths of an atmosphere, whereas that of sulphur is of the order of one-thousandth part of the millionth of an atmosphere.

The same phenomenon was exhibited in an even more striking manner by the following experiment:—Two equal bulbs A B (Fig. 16) were united by a tube containing a finely-ground stopcock C. A small piece of pure sulphur was put into A, and a small quantity of mercury into B, and the whole exhausted through the side-tube D by either a mercury pump or by the use of charcoal cooled in liquid air. While the exhaustion was going on the sulphur in A was fused, and finally the tube D was sealed off. On shutting the stopcock C, and allowing the apparatus to stand for some time, the application of a liquid air sponge to any part of the bulb B at once caused the deposition of a mercury mirror, which disappeared on allowing the cooled spot to regain the ordinary temperature. If the same cooling is applied to any part of the bulb A, no deposit takes place; but, if the sulphur has been recently fused so as to get it deposited on a portion of the glass surface in what is called the *utricular* state, then, in a short time a fine film of highly refracting sulphur is seen to have distilled to the cooled part, just like what takes place with the mercury in the other bulb. Now let the stopcock C be opened for a few seconds and shut again, and the local liquid air cooling on parts of both A and B repeated. On the cooled part of B nothing but mercury will be deposited as before; but on the cooled part of A a brilliant metallic deposit will be noticed, which is, however, not wholly mercury, for, on heating it with the finger, it is only partially volatilised, the portion which remains being sulphide of mercury. On repeating the operation on another part of A, in about a quarter of an hour all metallic deposition has disappeared. Thus, mercury vapour requires time to react with sulphur, but ultimately all the mercury vapour is removed by the sulphur. The apparatus enables the experiment to be repeated at any time.

Shortly after the discovery of oxygen by Priestley some Dutch physicists began the study of the gases absorbed and given off by living plants; and for this purpose the plants were covered by bell-jars whose lower edge was laid in a channel of mercury. But a difficulty arose, as it was found that the plants in these circumstances soon became sickly and died. Then the remarkable discovery was made that if sulphur was sprinkled over the leaves and the surface of the vessel, the deleterious effect of the mercury was overcome and the plants became healthy. Boussingault repeated and confirmed these results in 1868, and made many experiments to elucidate the remedial action of sulphur. He explained this action by pointing out that the poisoning of the plants arose from the presence of mercury vapour, and that as one volume of sulphur vapour was able to combine with six volumes of mercury vapour, the sulphur, although less volatile, was able effectually to neutralise the deleterious effects of the mercury vapour.

Now, the ratio of the pressure of mercury vapour to that of sulphur at the temperature of 115° C., when both bodies are in the liquid condition, is as 10 to 1. Seeing the sulphur molecule is S_6 to S_8, one volume of sulphur vapour is sufficient to neutralise or combine with six to eight volumes of mercury vapour, so that an excess of mercury pressure of from six to eight times that of the sulphur vapour can always be removed by combination with the sulphur. If, on the other hand, we compare the relative pressures of mercury at 100° C. to that of solid prismatic sulphur at the same temperature, this ratio is 37 to 1, so that the removal of the mercury vapour at the ordinary temperature, when the pressure ratio is still higher, cannot be fully explained. The effect of air and water vapour complicates the action in the case of plants, as the molecules of sulphur and mercury have not the free play they have when no inert gas is present. It would seem that in high vacua the S_2 molecule of sulphur may be considered as produced by molecular dissociation, and that moving with great rapidity relatively to the mercury

* A Discourse delivered at the Royal Institution, June 8, 1906.

gas molecules soon gets at the surface of the liquid mercury and coats it with a thin layer of mercury sulphide, which acts as a trap, stopping the exit of further mercury molecules. The effect of such a coating in preventing the escape of mercury vapour may be shown by the use of an inverted boiling-point flask like Fig. 17 containing a layer of fused sulphur at B, and mercury at A. Before and during very complete exhaustion, the mercury at A is kept in liquid air, and finally the flask is sealed off at C. On standing at the ordinary temperature, the surface of the mercury gets acted upon by the sulphur, and if the mercury is not shaken so as to crack the film of mercury sulphide, a little sponge of liquid air placed upon the surface at D shows no metallic deposit; but the moment the mercury is slightly shaken to break the surface film of the liquid mercury, metallic deposit is instantly formed by the local cooling.

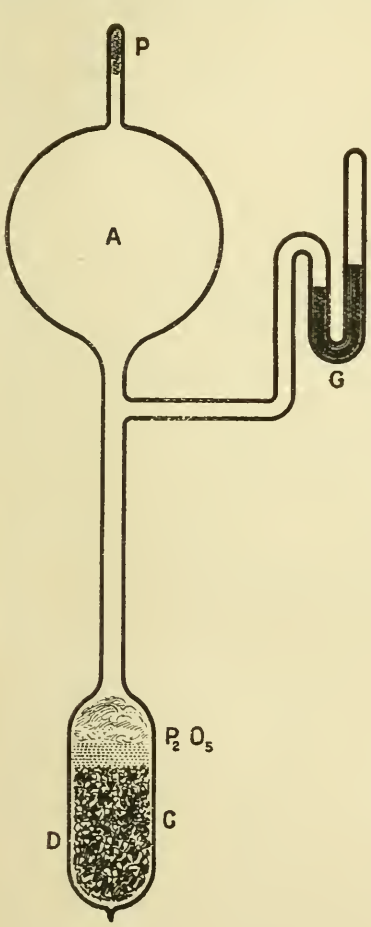


Fig. 18.

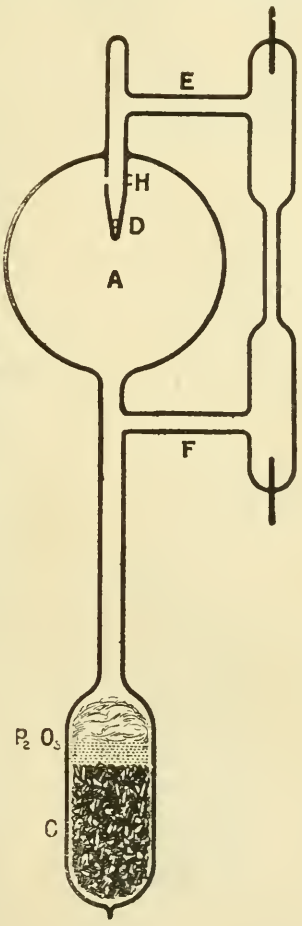


Fig. 19.

This deposit is not all mercury, but partly sulphide, because on taking away the sponge and heating the cooled spot by contact with the hand, a permanent brown part remains, whereas, if it had been all mercury it would have completely volatilised. On standing for a little time the liquid air cooling causes no metallic mirror, as all the mercury vapour has been removed by combination with the sulphur, and the sulphide film reforms on the mercury, when the experiment may be repeated.

Oxidation of Phosphorus in High Vacua.

In the Friday Evening Address of 1905 an experiment was shown illustrative of the well-known fact that the phosphorous glow caused by oxidation does not take place in dry oxygen at atmospheric pressure, and that it was only when the pressure was very considerably reduced that such action took place. This may be shown more clearly in the following way:—A globe (Fig. 18), A, has a small capillary-side tube, P, attached, containing a little phosphorus, that has been melted at its end, and is at the same time connected by another tube to a reservoir, D, containing charcoal covered with a layer of phosphoric anhydride to absorb all traces of moisture. To the side of this tube a small mercury gauge, G, is attached. After the whole vessel is thoroughly exhausted it is filled up to atmospheric pressure with pure oxygen gas, and the whole sealed off. On immersing the charcoal bulb in liquid air the pressure falls rapidly to a fraction of a millimetre pressure, and soon the globe A becomes filled with a phosphorescent glow, showing that chemical action is taking place. As the absorption of the oxygen by the charcoal continues the phosphorescence becomes less, and at last disappears, nothing finally filling the bulb but the vapour of phosphorus as it distils from P into the liquid air condenser. Meanwhile the gauge G shows that the pressure at which the phosphorescence begins must be only a fraction of a millimetre, and that it continues at a pressure below what could be measured on the gauge. When the charcoal is taken out of the liquid air, and the temperature allowed to rise, the course of the experiment is inverted, the oxygen occluded in the charcoal being given off, and as it meets the vapour of phosphorus in the bulb A, suddenly combines with it in a few oscillating flashes, and soon all is dark again. The experiment may be repeated after weeks of keeping with the same uniform results. The same thing is also very beautifully shown by the arrangement in Fig. 19. Here the gauge is replaced by a sparking tube B, having free access to the globe A by the tubes E and F, the former having communication by means of the small hole H; D is the phosphorus. The high vacuum at which the glow takes place in the bulb is shown by the character of the discharge taking place in B. A curious phenomenon is observed on stopping the electric discharge; now the glow travels from the bulb along E and F, and meets in the middle of B. It looks as if the electric discharge expelled all the phosphorus vapour from the discharge tube, and that the moving phosphorescent stream is due to the vapour of phosphorus coming back again. While the electric discharge is passing in B, the spectroscope reveals only the oxygen bands.

Separation of the Volatile Gases Neon, Hydrogen, Helium.

Attention has already been called to the selective nature of the absorption when a mixture of gases is presented to cooled charcoal, and it has been noted that the gas obtained from the charcoal after absorption of air has the quantity of oxygen increased from 21 to 50 or 60 per cent, The general law of this absorption is that the lower the boiling-point, in other words, the more volatile or less condensable the gas, the less is the absorption. Thus for air, nitrogen with the lower boiling-point is not absorbed to so great a degree as oxygen, which has the higher boiling-point. This is beautifully shown in the following experiment:—A number of spectroscopic tubes connected in

series with a large charcoal U-tube, are highly exhausted by cooled charcoal so that the discharge will hardly pass. The charcoal tube is now placed in liquid air, and a slow current of air is allowed to enter the system. The less volatile gases, oxygen, nitrogen, argon, are absorbed by the charcoal, while the more volatile gases, helium, neon, and hydrogen, are allowed to pass. In a short time, when the pressure of the latter gases has risen sufficiently, the first tube begins to glow with the well-known rich orange hue of neon. As the air-absorption progresses, the characteristic discharge of neon and helium gradually extends to the other tubes, the slowness of the current

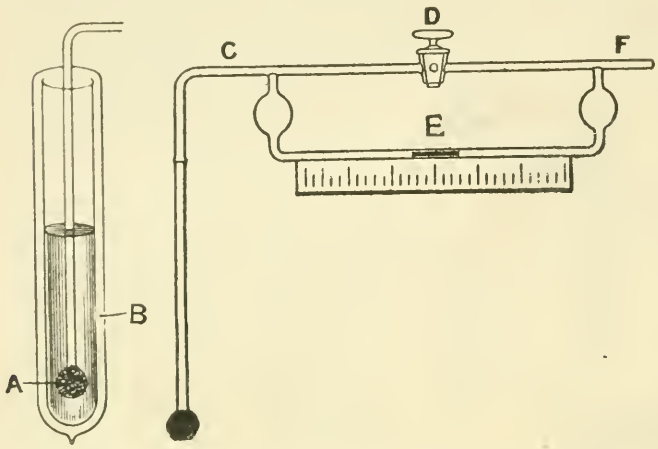


Fig. 20.

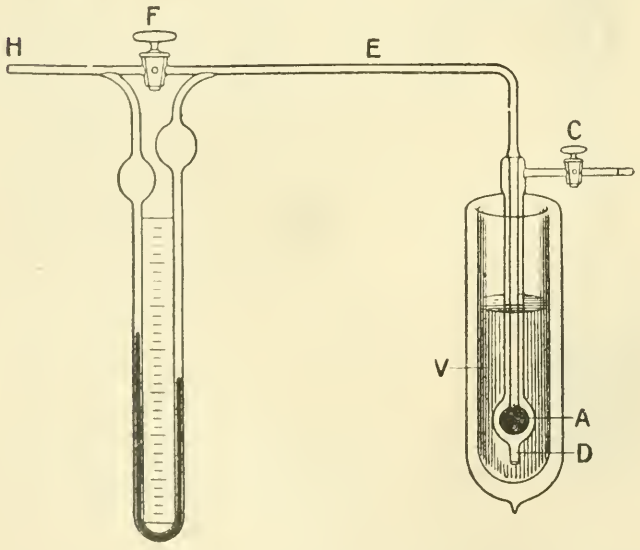


Fig. 21.

displaying vividly the march of the neon and helium glow. In this connection the sensitivity of the neon tube to induced electric oscillations from a coil of wire placed at right angles to the tube, was shown. This property of neon Professor Fleming makes use of in his ingenious wave-detector for wireless telegraphy—the cymometer.

The most volatile gases being neon, hydrogen, and helium, when a charcoal bulb attached to a sparking tube filled with helium was placed in liquid air, the nature of the luminosity remained unchanged, thus indicating that hardly any absorption had taken place at the temperature of liquid air. But on replacing the liquid air by liquid hydrogen under exhaustion, the pressure was so much reduced that the discharge no longer passed. This observation corroborates the statement already made that the boiling-point of hydrogen is a temperature for helium which corresponds with the boiling-point of air for hydrogen, and leads us to infer that the boiling-point of helium is about 5° to 6° absolute.

Measurements made in 1902, by what was called the float-method of separation, showed that the atmosphere contained as a minimum one part in 70,000 of neon, and one part in 362,000 of helium. Recent determinations by the charcoal method, made by Sir William Ramsay, give these proportions as one part in 80,790 of neon and one part in 245,300 of helium, or one part in 61,000 of both these gases together. The absorption of 30 litres of air by 500 grms. of charcoal gives a residuary pressure amounting to between 1·4 and 1·5 mm. of mercury pressure; thus representing a partial pressure of unabsorbed gases—helium, neon, and hydrogen—amounting to 1/5300 of the volume of the original air used in the experiment.

Separation of the Less Volatile Gases, Krypton and Xenon, by Charcoal.

The method of separating carbonic acid from air shown in the Friday Evening Address for 1905 is equally applicable to the separation of krypton and xenon. A current of air passes through a series of tubes immersed in liquid air for the purpose of purification, the final tube containing cotton-wool in order to retain any dust of the solid condensed impurities. This pure air is passed through a tube containing about 100 grms. of charcoal, the current being maintained for at least twenty-four hours. The charcoal tube is now removed and placed in solid carbonic acid, any gas coming off being allowed to escape. The gas remaining in the charcoal at −78° C. is now got out by heating and exhaustion, and all the carbon compounds and oxygen removed from it. The remaining gas, nitrogen containing krypton and xenon, is separated into its constituents by condensation and fractionation. Instead of passing a current of air over charcoal at −183° C., a few hundred grms. of charcoal may be covered with old liquid air, and the latter allowed to evaporate in a silver vacuum vessel, the gases remaining in the charcoal being separated as above. In this way krypton and xenon are readily separated from air and spectrum tubes easily prepared.

Charcoal Thermometer and Calorimeter.

Charcoal saturated with gases at low temperatures may be used as a thermoscope or calorimeter. Attention has been called to the law of absorption, that when the volume is constant, the pressure falls very rapidly with the temperature; in fact, the curve connecting them, when pressure is plotted as ordinate to temperature as abscissa, drops almost vertically as the temperature diminishes to the absolute zero, and a similar relation holds for the volume absorption at constant pressure. Hence, a small change of temperature is accompanied by a great change of pressure or volume absorption as the case may be. This was exemplified in the following experiment:—A charcoal bulb A (Fig. 20) previously saturated with air at −185° C. or hydrogen at −253° C. at any required pressure, the most convenient being atmospheric pressure, was immersed in a bath, B, of the corresponding liquefied gas

contained in a vacuum-jacketed vessel; and a tube, C, was led from it to a Leslie thermometer containing a sulphuric acid cylinder used as a registration instrument for volume. The gauge consisting of a U-tube, with bulbs on each side, to prevent any sudden sucking back of the drop of sulphuric acid, E, renders visible the slightest alteration of the volume of gas occluded in the charcoal. The upper ends of the U-tube were connected by a by-pass containing a stopcock D. On shutting this stopcock after the complete saturation of the charcoal with air has been effected, equilibrium of pressure between C and F could be obtained, while the sulphuric acid drop E occupied a convenient position in the gauge. On the approach of a candle-flame to the charcoal bulb, the gauge immediately showed a considerable expansion, notwithstanding that the radiant heat had to traverse a considerable quantity of liquefied gas and several thicknesses of glass tubing. In the same manner a beam of light thrown on the charcoal bulb when charged with hydrogen instead of air immediately affected the gauge in a striking way.

The apparatus can be rendered still more sensitive by the following device (Fig. 21):—The charcoal bulb, A, saturated with air at - 185° C., is surrounded with another larger bulb giving an annular space that can be filled with

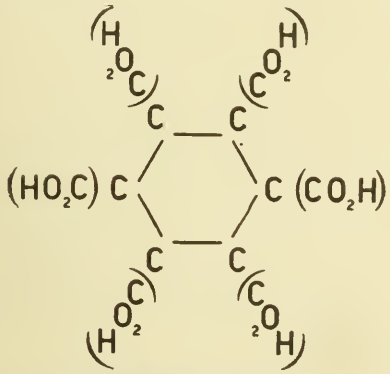


Fig. 22.—Graphical Formula of Mellitic Acid.

liquid air by opening the stopcock C, the orifice D being open while immersed in a large vacuum-jacketed reservoir, V, of liquid air. The tube E leading from A passes to a sulphuric acid manometer, with by-pass and stopcock, F, as before, thence to the open end, H. The apparatus works thus:—Before the radiant beam is turned on A, the annular space between the bulbs is cleared of liquid by blowing a little air through the tube C, and shutting the stopcock, thus forcing the liquid air out by the aperture D. The charcoal bulb is now surrounded by an atmosphere of liquid air vapour, or hydrogen, as the case may be, maintained at the boiling-point by the liquid in V. In these circumstances the maximum effect of any heat given to the charcoal bulb is obtained. The effects are magnified two or three times compared with those given by the charcoal bulb left in direct contact with the liquid.

The special value of this instrument for thermometric measurements is that it becomes more sensitive as the temperature falls, thus placing in our hands a most efficient thermometer for the lowest temperatures which can possibly be reached. Thus, when the charcoal is saturated with hydrogen gas at the boiling-point of hydrogen, the instrument has its maximum delicacy under ordinary circumstances; but provided helium was absorbed in charcoal at and below the temperature of solid hydrogen, then we can predict that the instrument would be still more sensitive to radiant energy.

If, further, the charcoal occupies an annular space surrounding another smaller bulb, into the interior of which any small heated object is inserted, the apparatus becomes a very sensitive calorimeter.

Much investigation is still necessary to clear up the nature of the various charcoals and their properties. One chemical character they possess, and that is that, by powerful oxidising agents like concentrated nitric acid or permanganate of potash, they seem all capable of giving a greater or less yield of an acid called mellitic acid, the graphical formula of which is represented in Fig. 22, which occurs in nature as the aluminium salt commonly called honeystone. This acid, we know, is a derivative of benzol, and its production from charcoal suggests that the latter has a structure of double benzine rings, each containing twelve atoms of carbon, such as is shown in Fig. 23. This gives a fundamental molecule containing a

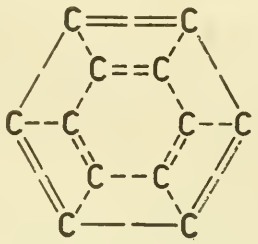


Fig. 23.—Graphical Formula of Charcoal Molecule.

large number of latent valences available for chemical or physical combination, and this structure may have something to do with the general absorptive power of charcoal.

The Professor thanked his assistants, Mr. R. N. Lennox and Mr. J. W. Heath, for valuable aid in the conduct of these experiments.

A METHOD OF DEPOSITING COPPER UPON GLASS FROM AQUEOUS SOLUTIONS IN A THIN BRILLIANTLY REFLECTING FILM, AND THUS PRODUCING A COPPER MIRROR.*

By F. D. CHATTAWAY, F.R.S.

Many organic substances which undergo oxidation easily are able to reduce various metallic oxides. The oxygen is removed with very different degrees of readiness, and the property is in consequence often used as a means of recognising particular compounds or atomic groupings.

Silver oxide is especially easily reduced, and if it is dissolved in an aqueous solution of ammonia the metal, by an appropriate agent, as Liebig first observed (*Annalen*, 1835, xiv., 133), may be obtained attached to the glass walls of the containing vessel as a brilliant reflecting film.

This observation has received an important industrial application in the manufacture of mirrors, and silver thus deposited has now practically replaced the tin amalgam formerly used, which so often seriously affected the health of the workers.

With the view of improving the processes originally used, many chemists have studied the conditions under which glass is coated with silver, but their investigations have generally had for their object the preparation of a liquid which would deposit a uniform and coherent layer of the metal over a large glass surface at the ordinary temperature. Liebig (*Annalen*, 1856, xcviii., 132) was the first to solve the problem satisfactorily, and his method, in which milk sugar is the reducing agent, was formerly extensively used.

Other metals are not so easily laid down upon glass in a firm reflecting film as is silver, and in particular copper, which is so closely related to it, is not in similar cir-

* A Paper read before the Royal Society, November 21, 1907.

cumstances so deposited. Metallic copper has been attached to glass in various ways. Faraday (*Phil. Trans.*, 1857, p. 145), about the time when silver mirrors were attracting much attention, made the interesting observation that a mirror-like deposit of the metal upon glass having the proper metallic lustre and colour by reflection could be obtained by disssolving a little oxide of copper in olive oil and heating plates of glass in a bath of this liquid up to the decomposing temperature of the oil. Mirrors, however, obtained by Faraday's method, if of any size, are liable to be stained and discoloured in patches by decomposition products of the oil, and they are, moreover, generally lacking in brilliancy. Further, as the deposition of the metal only takes place at a temperature above that at which the oil decomposes, the process is excessively disagreeable to carry out, and, as the oil is spoiled, it is somewhat costly.

Faraday also discovered (*Phil. Trans.*, 1857, p. 154) that a fine deposit of copper upon glass could be produced by deflagrating the metal in the neighbourhood of the glass by a Leyden battery in an atmosphere of hydrogen, and Wright, employing a method essentially the same (Silliman, *Amer. Journ.*, 1877, [3]. xiii., 49), obtained small brilliant mirrors of copper on the inner surface of exhausted glass tubes by passing through them an electric discharge between copper electrodes.

Everyone who has reduced Fehling's solution with excess of grape sugar must have noticed that occasionally the metal produced adheres to the sides of the beaker or flask in somewhat reflecting patches, and much brighter patches are obtained when certain copper salts such as formate or acetate are heated in glass vessels. The firm of Weisskopf, in Morchenstein, has further succeeded in depositing copper upon glass by reducing the hydroxide in presence of zinc chloride together with gold or platinum chloride by a somewhat complicated liquid mixture containing cane-sugar, glycerin, and formaldehyde.

These facts lead to the conclusion that copper should be capable of deposition in the same way as silver, if a suitable reducing agent were forthcoming; this I have recently found in phenylhydrazine.

Phenylhydrazine, as I have elsewhere showed (*Trans. Chem. Soc.*, 1907), especially in presence of caustic potash, which greatly accelerates the action, is easily oxidised by free oxygen, there being produced in all likelihood hydroxyphenylhydrazine, which immediately breaks down into a molecule of benzene, a molecule of nitrogen, and a molecule of water thus:—

$$\begin{matrix} C_6H_5{-}N{-}H \\ | \\ H{-}N{-}H \end{matrix} + O = \begin{matrix} C_6H_5{-}N{-}H \\ | \\ H{-}N{-}OH \end{matrix} = C_6H_6 + N_2 + H_2O.$$

Copper oxide acts similarly upon the base, and under suitable conditions the metal can be deposited upon glass in the form of a fine mirror.

The operation may be carried out in a variety of ways, using finely divided black copper oxide suspended in a boiling saturated solution of phenylhydrazine or a liquid made by mixing the latter with a solution of copper hydroxide in alkaline tartrates or ammonia.

The following procedure, which resembles that employed in silvering glass, gives a uniformly excellent result:—Heat a mixture of one part of freshly distilled phenylhydrazine and two parts of water till a clear solution is obtained. To this add about half its bulk of a warm saturated solution of cupric hydroxide in strong ammonia. Nitrogen is freely evolved during the addition, and the cupric is reduced to cuprous hydroxide, which remains dissolved in the ammoniacal liquid, and does not undergo any immediate appreciable further reduction until heated. Add next a hot 10 per cent solution of potassium hydroxide until a slight permanent precipitate of cuprous hydroxide is produced. If this colourless or pale yellow liquid be cautiously heated in contact with a perfectly clean glass surface, metallic copper is deposited upon it in the form of a thin coherent perfectly reflecting lamina.

As nitrogen is evolved during the reduction, and as tarry by-products are formed in small quantity and float with the benzene produced to the surface of the liquid, if flasks or tubes are to be coppered, devices have to be adopted to keep the inner surface completely covered by the liquid from which the metal is being deposited, whilst allowing the gas to escape.

If the glass in any part is not perfectly coated, the process may be repeated, but a uniform deposit is seldom obtained unless the whole surface is covered in one operation. To obtain a film of sufficient thickness to be permanent, and to prevent its superficial oxidation, it is best to allow it to remain for an hour or so in contact with the warm reducing fluid, and not to pour this off till it has cooled to the temperature of the air. The surface of the deposited copper should then be well washed, first with water, and afterwards with alcohol and ether, and finally should be protected from the slow oxidising action of the air by one or two coats of some quick-drying varnish.

Very little of the phenylhydrazine is actually used up in the reduction, and the same fluid may be employed again and again after filtering while warm through cotton-wool and mixing with more solution of copper hydroxide, adding fresh phenylhydrazine when necessary to compensate for the dilution. If required for future use, the liquid must be kept in a stoppered bottle carefully protected from the air, as free oxygen is very readily absorbed by it and the phenylhydrazine thereby destroyed.

The mirrors obtained by this method are very beautiful, for they show the pleasing red colour of copper, and are as perfect in reflecting surface and as lustrous as the similar mirrors obtained by the deposition of silver.

To carry out the operation successfully, it is essential to cleanse very thoroughly the surface of the glass; this is best done by well rubbing in turn with a strong solution of soap, with strong nitric acid, and with strong caustic potash, using a pad of cotton-wool soaked in these liquids, and washing well between the successive operations.

Surfaces of blown glass are more readily coated with copper than polished surfaces. In any case old glass should not be used, at least without the surface being carefully re-polished.

Ammonia in excess hinders the deposition of copper, as it does that of silver, while caustic alkali accelerates it.

It is interesting to note that the copper is in the monovalent or cuprous state, in which it is analogous to silver, when it shows a similar tendency to be deposited in a metallic film upon glass.

Little is known as to the reasons why, when metallic oxides are reduced in aqueous solutions, the metals under certain conditions are deposited upon glass in a thin reflecting lamina, while under others, apparently equally favourable to such deposition, they separate in a spongy or flocculent state. Vogel (*Journ. Prakt. Chem.*, 1862, lxxxvi., 321) concludes from his experiments with silver oxide that when complete reduction takes place in one stage, a mirror or crystalline deposit is obtained, whilst granular or finely-divided silver is produced in two stages, a lower insoluble oxide separating as the primary product of the reduction, and being afterwards itself further reduced.

The behaviour of copper oxide on reduction makes it, however, very improbable that the various stages of the process affect the result.

For the production of a mirror it appears rather to be essential that the compound undergoing reduction shall be in solution, and that its concentration shall be small, that the liquid in which it takes place shall be alkaline, and that action shall be more rapid at the surface of the glass than elsewhere.

It is certain that the nature of the surface on which the metal is deposited plays an important part in the process, since both silver and copper are deposited much better upon blown than upon polished glass and upon surfaces which have not for long been exposed to the action of the air or of water.

It seems probable that the glass surface itself acts a catalyser and locally accelerates the action.

Oberbeck, some years ago, measured the electric resistances of a number of silver films deposited upon glass from aqueous solution (*Ann. der Physik und Chemie*, 1892, p. 282).

He made the interesting discovery that such resistances, although very large immediately after the metal had been deposited, continually diminished with time, and although a minimum was not reached in two years, ultimately approximated to the resistances which would have been shown by films of ordinary silver of corresponding thickness and size. The films during this change of resistance altered neither in reflecting power nor in appearance when viewed by transmitted light.

As reflecting silver films of very different thickness and initial resistance and produced under very different conditions all showed this great increase in conductivity, Oberbeck concluded that when silver is first deposited from aqueous solution in the form of a mirror, it is in a different molecular condition from ordinary silver, but that in time its state approaches that of the latter more and more.

THE RAPID DETERMINATION OF NICKEL IN THE PRESENCE OF CHROMIUM, IRON, AND MANGANESE.

By C. M. JOHNSON.

In applying the method of T. Moore (Chemical News, lxxii., 92) to the determination of nickel in steel, the directions given by Brearley and Ibbotson on p. 183, "Analysis of Steel Works Materials," were followed:—One grm. of steel was dissolved in a 150 cc. beaker with 10 cc. of concentrated hydrochloric acid diluted with an equal volume of water.

When action ceased 10 cc. of nitric acid (1·20) were added and the contents of the beaker were boiled to about one-half. 16 cc. of dilute sulphuric acid were poured into the solution and also 3 grms. of powdered citric acid. The solution was stirred until the citric acid was dissolved, transferred to a 600 cc. beaker, and rendered faintly but distinctly ammoniacal.

The nickel was titrated with a standard solution of potassium cyanide, using a measured amount of standard silver nitrate and 2 cc. of a 20 per cent solution of potassium iodide as an indicator. The deep red colour of the citrate of iron greatly obscures the end-point. The authors complain of this colour and recommend the use of a condensing lens to cast a beam of light through the darkness. In the presence of chromium the writer found that a still more sombre gloom settled down over the close of the reaction. The authors mentioned also state that this element retards the union of the cyanide and the nickel, causing the recurrence of the cloud of silver iodide.

After struggling with the process for some time and always carefully separating the chromium, and with it the iron, in chrome steels, an attempt was made to dispel the darkness and also to avoid these tedious separations:—Less citric acid per grm. of steel was taken and the dark red shaded to blackness.

Naturally, the amount of citric acid per grm. of steel was then increased, that is, 6 grms. of citric acid per grm. of steel were used, and a marked improvement was noted. Still more citric acid caused a complete lifting of the shadows.

The following modified procedure was finally adopted for nickel steels after having been thoroughly tested with plain carbon steels to which known amounts of nickel had been added: Dissolve 1 grm. of steel drillings in a 150 cc. beaker with 20 cc. of hydrochloric acid (1 : 1). When action ceases add 10 cc. of nitric acid (1·20).

Reduce the volume of the solution to about 15 cc., keeping the beaker covered during the boiling. Remove the beaker from the fire and pour into it 8 cc. of concentrated sulphuric acid diluted with 24 cc. of water. The presence of the sulphuric acid is essential to a sharp end reaction between the cyanide standard and the silver iodide in the subsequent titration.

Transfer the contents of the beaker to one of 600 cc., capacity containing 12 grms. of powdered citric acid. Stir until the citric acid is dissolved. Render this solution *faintly* but *distinctly* alkaline with ammonia, using one part of concentrated ammonia diluted with one part of water. A large excess of ammonia causes low results. Stand the beaker in running water until it is cold. The volume of the solution should now be about 300 cc. Much larger volumes than 300 cc. should be avoided, as great dilution retards the end-point, causing the cloud of silver iodide to disappear and then to reappear again in a few minutes.

The faintly ammoniacal condition can be easily controlled by adding the ammonia rather slowly and noting the changes of colour that ensue: The first change is to amber, then to yellowish-green, then to distinct green, then to a light shade of green, then to a yellow almost matching the yellow colour of the acid solution. The reappearance of the yellow tint indicates that alkalinity is nearly attained.

A little more ammonia now causes a brownish shade, which is evidence that the ammonia is in slight excess. The moderately alkaline citrate of iron obtained in the proportion of 1 grm. of iron to 12 grms. of the citric acid yields a bright greenish-yellow solution in plain nickel steels instead of being of a dense dark red shade!

To the cold solution, 2 cc. of a 20 per cent solution of potassium iodide are added. From a 50 cc. burette a standard solution of silver nitrate is dropped into the same beaker, producing with the iodide a white turbidity. The standard potassium cyanide is added with constant stirring until the cloud of silver iodide just disappears, which it does on being converted into silver cyanide. Nickel cyanide is first formed and then the silver cyanide is produced:—

1. $Ni(NO_3)_2 + 4KCN = Ni(CN)_2.2KCN + 2KNO_3$;
2. $AgNO_3 + 2KCN = AgCN.KCN + KNO_3$.

If the directions are followed as given, the titration can be accomplished at almost the full speed of the burette. If the titrated solutions are permitted to remain in the open beakers for a time, a film usually appears on the surface of the liquid. No account is taken of it as its presence is most likely due to a superficial loss of ammonia. The reactions are always found to be completed when the body of the solution is freed of the iodide precipitate.

Standards.—From the equations as given, 5·85 grms. of silver nitrate are equivalent to 4·4868 grms. of potassium cyanide. This weight of cyanide dissolved in one litre of water gives a value of 1 cc. equals about 0·001014 grm. of nickel.

As comparatively little silver nitrate is needed with each analysis, it is not advisable to prepare more than a-half litre of the water solution of this salt, using 2·925 grms. per 500 cc. of distilled water.

The potassium cyanide standard should contain about 5 grms. of potassium hydroxide to the litre, which renders it quite permanent. The solutions are readily standardised by applying them to a plain steel to which a known amount of nickel has been added. The chemically pure double sulphate of nickel and ammonium is a convenient standardising medium. For example, 0·2 grm. and 0·25 grm. of the double sulphate can be weighed into 150 cc. beakers together with 1 grm. of plain carbon steel drillings.

This mixture is then put through all of the foregoing manipulations and titrated with the cyanide solution that is to be standardised. The number of cc. of the silver nitrate and of the potassium cyanide solution used in this titration are noted. An excess of 10 cc. of the cyanide is now added and in turn titrated with the silver nitrate solution until a distinct cloud of silver iodide is produced.

This second titration gives the relation between the silver solution and the cyanide.

An actual case will illustrate the calculations :—In Sample No. 3477, 1·7 cc. of standard silver nitrate solution were required to produce a distinct turbidity and also to combine with any excess of potassium cyanide standard. In all 35 cc. of the cyanide were consumed in the titration. When the cloud of silver iodide had just been dispelled an excess of 9·8 cc. of cyanide was allowed to flow into the clear solution. Just 10·1 cc. of silver nitrate standard were needed to produce a reappearance of the cloudiness. Therefore $9·8 \div 10·1 = 0·97$, or 0·97 cc. of cyanide standard solution equals 1 cc. of silver nitrate. Hence instead of deducting 1·7 cc. from 35 cc., $1·7 \times 0·97$ or 1·65 cc. were deducted, leaving 33·35 cc. of cyanide combined with the nickel in this steel.

To a plain carbon steel 0·200 grm. of double sulphate of nickel and ammonium were added, put through all of the steps of a regular analysis. This mixture required 28·75 cc. of cyanide. The nickel salt contains 14·86 per cent of nickel or $0·200 + 0·1486 = 0·02972$ grm. of nickel were present. Hence $0·02972 \div 28·75 = 0·00103$ or 1 cc. of standard cyanide solution is equivalent to 0·00103 grm. of nickel. No. 3477, as has been stated, required 33·35 cc. of the cyanide standard, and therefore contains $0·00103 \times 33·35 = 0·03435$ or 0·03435 grm. of nickel or 3·435 per cent.

Chromium-Nickel Steels.—When chromium is present proceed exactly as in plain nickel steels except that 24 grms. of citric acid per grm. of steel are used. This proportion of citric acid is adequate to render the end-point quite as easy to see as in ordinary nickel steels. The action is prompt and free from recurrence of turbidity. Of course cloudiness through the entire solution will occur, as the ammonia is dissipated from it, after it has stood for some time in an open beaker.

Table I. furnishes satisfactory proof that chromium does not interfere with the successful technical estimation of nickel in its presence.

TABLE I.

Sample No.	No chromium added. Nickel found, per cent.	Per cent of chromium added to a portion of the same steels.	Nickel found after the addition of varying amounts of chromium.
525	5·09	4·0	5·10
2991	4·44	2·0	4·45
7239	3·24	1·0	3·28
3017	4·96	1·0	5·03
612	3·47	0·5	3·47
7273	3·29	1·0	3·31
622	3·56	0·5	3·56
7288	3·32	2·0	3·41
7289	3·11	2·0	3·16
663	3·57	6·0	3·59
2991	4·44	3·0	4·47

The chromium was introduced in the form of re-crystallised chemically pure potassium dichromate. The dichromate crystals were mixed with a weighed amount of nickel steel drillings before the addition of the 20 cc. of hydrochloric acid. The combined action of the nascent hydrogen from the steel, the excess of boiling hydrochloric acid, and the ferrous chloride reduced the chromate to chromic chloride, thus duplicating the conditions found when a chromium-nickel is similarly treated.

Determinations by this modification of the cyanide method can be finished in from forty-five to fifty minutes, either in the presence or absence of any per cent of chromium likely to be met with in steels or alloys soluble in the acids given. In this laboratory *duplicate* determinations in nickel or nickel-chromium steels are made in the time just specified. By the process one can decide in a few minutes whether or not nickel is present in a given steel and just how much. Tungsten, if present, does not interfere appreciably, as has been noted by the authors mentioned in this article. The writer had two different amounts of nickel added to a steel containing several per cent of chromium and 16—17 per cent of tungsten. This steel was then carried through exactly as though no tungsten or chromium were present, using the method as given for chromium-nickel steel.

Nickel added (grm.) ..	0·0297	0·03715	None
Nickel found	0·0299	0·0372	0·0006

Tests were then made in the same manner in the presence of molybdenum and vanadium as follows :—

TABLE II.

Name.	Kind of steel or mixture.	Nickel added. Grm.	Nickel found. Grm.
J. R. steel . .	Contains 10 per cent ± Mo	0·0297	0·0295
		0·0222	0·0223
		None	0·0002
Bxx—173 steel .	Contains 4 per cent Mo and 4 per cent Cr	0·0223	0·0222
		0·0297	0·0296
		None	0·0004
A mixture . .	0·920 grm. of steel ..	0·0297	0·0298
	0·030 „ nickel ..		
	0·018 „ vanadium		
A mixture . .	0·840 „ steel ..	0·0223	0·0227
	0·022 „ nickel ..		
	0·035 „ vanadium		
A blank	1·000 „ steel ..	None	0·0008
	0·035 „ vanadium		

Table II. demonstrates that neither vanadium, tungsten, chromium, nor molybdenum, when present in the amounts given, interferes appreciably in technical analysis. These amounts represent extreme cases, especially for the vanadium, it being equivalent in one instance to 3·5 per cent V when 1 grm. of steel is taken.

As copper also forms cyanides, its presence would cause results to be too high, but copper is religiously avoided in good steel making. Its presence is extremely unlikely in greater amounts than 0·06 per cent, although the writer, on one occasion, found as much as 0·25 per cent in a low carbon steel, not a *crucible* steel, however. Crucible steel rarely contains over 0·04 per cent copper. The choice brands are under 0·02 per cent in copper.

Wishing to test the extent to which nickel could be titrated in the presence of large percentages of chromium, iron being also present, the mixtures as given in Table III. were titrated with potassium cyanide. The various salts were weighed into 150 cc. beakers, together with the proper amounts of steel drillings. The same proportions of hydrochloric, nitric, citric, and sulphuric acids were employed as are herein given for nickel-chromium steels, and were applied in the same manner.

A sufficient quantity of the salts of chromium and nickel, and of the steel drillings, were taken to give a total of one-half grm. of metals in the mixture.

Double sulphate of nickel and ammonium $[(NH_4)_2SO_4.NiSO_4.6H_2O]$, potassium dichromate, and steel drillings free from nickel were used as sources of nickel, chromium, and iron, respectively.

To obtain the nickel value of the cyanide standard under conditions similar to those existing in the mixtures tested, standardising mixtures of these salts were prepared varying from the mixtures tested as much as 1 per cent to 20 per cent in the different constituents.

For mixtures exceeding 10 per cent of nickel, a standard cyanide solution with a nickel value of 1 cc. = 0·0031 grm. of nickel was used. The standardising mixtures were dissolved and treated exactly as the mixtures tested. The same method of standardisation was observed in the work recorded in Table IV.

Table III.

Per cent of metals. Ni.	Cr.	Fe.	Grm. of nickel added.	Grm. of nickel found.	
30	40	30	0·1499	0·1494	0·1495
60	20	20	0·2999	0·3003	0·2989
20	40	40	0·1029	0·1022	—
5	90	5	0·0250	0·0248	0·0244
4	92	4	0·0200	0·0199	—
1·5	95	3·5	0·00749	0·00805	0·00822
0·5	99	0·5	0·00249	0·00225 0·00247	0·00243 0·0026
0	98·9	1·0	None	None	

Table III. demonstrates that nickel may be estimated by the foregoing modified cyanide process, using the proportions of citric acid as given, with sufficient accuracy for works analysis, and indeed for most practical purposes; even when the percentage of chromium is as much as 99 per cent, and the nickel content is but one-half of 1 per cent.

The titration of the mixtures given in Table III., and containing the larger amounts of chromium, requires considerable practice on the part of the operator. The work should always be carried out in duplicate. The disappearance of the cloudiness in the presence of 0·100 to 0·450 grm. of chromium in a volume of 350—400 cc., is much more exactly observed when the mixture containing the iodide cloud is compared, from time to time, with a *similar* mixture which is perfectly free of this milky turbidity. The dilution of the deep purple, or wine colour, of these ammoniacal mixtures of citrates to more than 300 to 400 cc., renders the end-point but slightly more distinct, and has the great objection of retarding the reaction between the cyanide and the nickel. The increase above 24 grms. of citric acid in the solution, even to the extent of adding 60 grms. of citric acid, did not relieve the density of colour to any perceptible extent.

When titrating with a standard, 1 cc. of cyanide = 0·0031 grm. of nickel (three times the strength used for steels) do not also increase the strength of the silver standard to equal it, but still retain the silver nitrate standard as given for steels. A silver nitrate solution sufficiently concentrated to be equivalent, volume for volume, to the cyanide standard (1 cc. = 0·0031 grm. of nickel), on being dropped into the solution containing the potassium iodide, does not produce the usual opalescence alone, but also forms curds of iodide that do not readily combine with the cyanide standard. The end-point is reached and the main body of the solution is free of cloud while curds of silver iodide still lie on the bottom of the beaker. The weaker silver nitrate standard, or 5·85 grms. of silver nitrate to the litre, produces with the potassium iodide a finely divided cloud of precipitate that combines promptly with the strong cyanide standard, giving a sharp end-point. Weigh, therefore, 2·925 grms. of silver nitrate, diluting to 500 cc., and 13·4604 grms. of the best grade of potassium cyanide, diluting to 1000 cc., for titrations of solutions containing from 0·100 to 0·300 grm. of nickel; 1 cc. of this silver nitrate solution should be equivalent to one-third cc. of the concentrated cyanide standard (1 cc. cyanide = 0·0031 ± grms. of nickel).

The titration of nickel by potassium cyanide in mixtures containing large percentages of manganese with varying amounts of chromium and iron was also tried.

As in the experiments outlined in Table III., mixtures were prepared to contain one-half grm. of metallic substances. The same nickel and chromium salts were employed. Potassium permanganate crystals supplied the manganese.

The crystals of double sulphate of nickel and ammonium, potassium dichromate and potassium permanganate, were weighed into a 150 cc. beaker with the steel drillings. To this were added 20 cc. of dilute hydrochloric acid. The contents of the beaker were then boiled, after the first action was completed, until the chromate and permanganate were reduced. An addition of 10 cc. of nitric acid (1·20) followed, and the analysis was carried out exactly as given for chromium-nickel steels, using 24 grms. of citric acid. The results obtained are given in Table IV. Sulphuric acid was added as in the process for steels.

Table IV.

Per cent of metals. Ni.	Mn.	Cr.	Fe.	Grm of nickel. Added.	Found.
41	20	10	30	0·2059	0·2058
20·6	40	20	20	0·1029	0·10228
15	60	15	10	0·0750	0·0752
1·5	95·5	1	2	0·00749	0·00762
0·25	94·9	2	2·9	0·00124	0·00122
—	94·9	2	4	None	0·00006

Table IV. gives evidence of the fact that nickel can be accurately determined in the presence of large percentages of chromium and manganese, if the conditions herein given are carefully observed. In the hands of a practised operator no difficulty was experienced in the analysis when as much as 95 per cent of manganese was in solution with but 0·25 per cent of nickel.—*Journal of the American Chemical Society*, xxix., No. 8.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 23, December 2, 1907.

This number contains no chemical matter.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xl., No. 16, 1907.

Electrolytic Reduction of Ethyl Barbituric Acids.—Julius Tafel and Herbert Bryan Thompson.—When 5 . 5-diethyl barbituric acid (veronal) is reduced electrolytically only one crystalline substance is produced. This is 5 . 5-diethyl-4 . 6-dioxy-2 . 5-dihydropyrimidine—

$$\begin{matrix} NH—CO \\ \dot{C}H_2 \quad \dot{C}(C_2H_5)_2. \\ \dot{N}H—\dot{C}O \end{matrix}$$

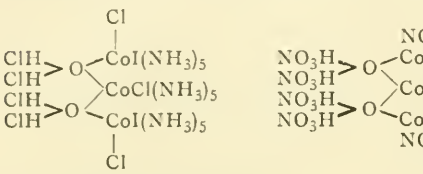
5-Monoethyl barbituric acid under the same circumstances yields 5-ethyl hydrouracyl and 5-ethyl trimethylene urea. It is much more easily reduced than the diethyl derivative. Barbituric acid itself yields hydrouracyl and trimethylene urea. This striking difference in the behaviour of barbituric acid and its monoethyl derivative on the one hand, and the diethyl derivative on the other, is undoubtedly due to the fact that in the two first compounds the malonyl carbonyl is much more easily reduced electrolytically than urea carbonyl, but that the introduction of a second ethyl group into the molecule makes the carbonyl of the carbon chain less easily reducible than the urea carbonyl.

Cobaltie Pentammins.—J. Sand and G. Bokman.—When nitric acid acts upon ammoniacal solutions of cobaltous salts two different series of compounds result. The salts of one group, the cobaltous-nitroso-pentammins, contain divalent cobalt and form glittering black crystals. These black compounds isomerise to the red cobaltic-nitroso-pentammins, which contain trivalent cobalt, and unlike the black compounds are very stable towards water. The black chloride and nitrate, when treated with alcoholic iodine solution, yield green substances which belong to a hitherto unknown type of condensed cobaltic pentammins. It was found that the iodide contained considerable

quantities of chlorine. The quantitative analysis of the substances leads to the following complicated formulæ :—

I. Precipitated with KI $Co_3I_2Cl(NH_3)_{15}I_6.2H_2O$
II. Precipitated with HNO_3 .. .. .. $Co_3I_2Cl(NH_3)_{15}(NO_3)_6.2H_2O$
III. Precipitated with HCl .. .. .. $Co_3I_2Cl(NH_3)_{15}(Cl_6.2H_2O$
IV. Black nitrate + I ; boiled with HNO_3 $Co_3I_2(NO_3)(NH_3)_{15}(NO_3)_6.2H_2O$

The conductivity of a freshly prepared solution of the green chloride III. was found to be three times as great as that of a ternary electrolyte. Hence this salt must contain to one cobalt atom two ionisable acid radicles. In the complex cation there are always present 2 I and 1 Cl to 3 Co, or 2 I and 1 NO_3, in non-ionogenic combination, as well as the fifteen purpureo ammonia residues. It is noteworthy that all four salts after being dried in vacuo contain 2 H_2O molecules for 3 Co. Probably these water molecules join the three cobalt atoms in the complex. The possible structural formulæ are—



Chloride III.
(*cf.* Iodide I., Nitrate II.).

Compounds of Tetravalent Molybdenum.—J. Sand and Johanna Maas.—The electrolytic reduction of molybdic acid in hydrogen sulphocyanide solution gives, besides sulphocyanides of pentavalent molybdenum, very complex salts in which a central molybdenum atom with four principal valencies is present. A very characteristic zinc salt, $[Mo(SCN)_6(NH_3)_4]Zn$, can be prepared by saturating the reduced solution with ammonia and precipitating the filtrate with ammoniacal zinc chloride solution. From this zinc salt a series of salts of the type $Mo(SCN)_6(NH_3)_3H_2$ can be obtained. Salts of this constitution yield addition products with acetic acid, ethyl alcohol, and propyl alcohol. The tetravalency of the molybdenum can be proved by heating weighed quantities of the zinc salt in carbon dioxide, cooling, adding manganese sulphate, and dilute sulphuric acid, and titrating the solution with permanganate.

MISCELLANEOUS.

The Andrew Carnegie Research Scholarship.—A Research Scholarship or Scholarships, of such value as may appear expedient to the Council of the Iron and Steel Institute from time to time, founded by Mr. Andrew Carnegie (Past-President), who has presented to the Iron and Steel Institute eighty-nine one-thousand dollar 5 per cent Debenture Bonds for the purpose, will be awarded annually, irrespective of sex or nationality, on the recommendation of the Council of the Institute. Candidates, who must be under thirty-five years of age, must apply on a special form before the end of February to the Secretary of the Institute. The object of this scheme of Scholarships is not to facilitate ordinary collegiate studies, but to enable students, who have passed through a college curriculum or have been trained in industrial establishments, to conduct researches in the metallurgy of iron and steel and allied subjects, with the view of aiding its advance or its application to industry. There is no restriction as to the place of research which may be selected, whether university, technical school, or works, provided it be properly equipped for the prosecution of metallurgical investigations. The appointment to a Scholarship shall be for one year, but the Council may at their discretion renew the Scholarship for a further period instead of proceeding to a new election. The results of the research shall be communicated to the Iron and Steel Institute in the form of a paper to be submitted to the Annual General Meeting of members, and if the Council consider the paper to be of sufficient merit, the Andrew Carnegie Gold Medal shall be awarded to its author. Should the paper in any year not be of sufficient merit, the medal will not be awarded in that year.

MEETINGS FOR THE WEEK.

Tuesday, 14th.—Royal Institution, 3. "The Internal Ear of different Animals," by Dr. A. E. Gray, F.R.S.E.

Wednesday, 15th.—Microscopical, 8. "The Microscope as an Aid to the Study of the Biology of Insects, with Special Reference to the Foods," by W. Wesché. An improved type of Mercury Vapour Lamp for Use with the Microscope will be exhibited and described by Mr. J. E. Barnard.

—— Society of Arts, 8. "Screen-plate Processes of Colour Photography," by Dr. C. E. K. Mees.

Thursday, 16th.—Royal Institution, 3. "The Building of Britain," by Prof. W. W. Watts, F.R.S., &c.

—— Society of Arts, 4.30. "Indian Agriculture," by Henry Stavely Lawrence, I.C.S.

Friday, 17th.—Royal Institution, 9. "The Centenary of Davy's Discovery of the Metals of the Alkalis," by Prof. T. E. Thorpe, C.B., F.R.S.

Saturday, 18th.—Royal Institution, 3. "The Electrification of Railways," by Prof. Gisbert Kapp, Dr.Eng., M.Inst. C.E.

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THE CHEMICAL NEWS.

Vol. XCVII., No. 2512.

THE ATOMIC WEIGHT OF TELLURIUM.

By W. MARCKWALD.

Ever since the periodic system of the elements was established the atomic weight of tellurium has repeatedly been the subject of thorough investigation, because it had been found to be higher than that of iodine, and thus the element did not fit in well with the system.

A. Gautbier (*Sitzungsber. d. Physik.-medizin. Soz. in Erlangen*, 1905, xxxvii., 270) has recently prepared a complete summary of all the publications which have appeared on this subject, and thus it is not necessary for me to go over the same ground again. I shall only touch upon the most important results.

The conversion of tellurium into the oxide by means of nitric acid is not satisfactory for the determination of the atomic weight. B. Brauner (*Monatsh. für Chem.*, 1898, x., 411) thinks that this is because tellurium dioxide does not give up the last traces of oxides of nitrogen until the temperature at which it begins to volatilise is reached (*cf.* also McIvor, Chemical News, 1903, lxxxviii., 17). He obtained results which agreed very well when he determined the bromine in tellurium tetrabromide by titration. His value was 127·71. This value was approximately confirmed by M. Chikasige (*Journ. Chem. Soc.*, 1896, lxix., 881) by the same method.

(Note.—All the results given in this paper are calculated with the values given in this year's Table of the International Atomic Weight Commission).

A greater number of workers have studied the quantitative transformation of tellurium dioxide into tellurium. Staudenmaier (*Zeit. Anorg. Chem.*, 1895, x., 189) effected the reduction by a current of hydrogen, and in two experiments, in which altogether only 3·5 grms. of substance were used, found a mean value of Te = 127·57. Almost the same number is obtained when the mean of G. Pellini's (*Ber.*, 1901, xxxiv., 3807) three results, obtained by the same method as Staudenmaier's, is calculated, but the numbers vary from 127·30 to 128·02. K. B. Heberlein (Inaugural Dissertation, Basel, 1898), employing the same reaction, obtained two concordant results, but the value was much lower, viz., 126·99, while Gutbier (*loc. cit.*) in five determinations found 127·55 to 127·68, which agreed best with Staudenmaier. Gutbier obtained almost the same result when he reduced tellurium dioxide in the wet way by means of hydrazine. The differences in the results of different observers are very remarkable. The material used, TeO_2, can easily be obtained pure. On the other hand, it is questionable whether the reduction in the dry way is complete, and whether the occlusion of hydrogen can be entirely prevented. The water formed in the reaction has unfortunately never been weighed.

The basic nitrate, $(TeO_2)_2HNO_3$, which can be converted into dioxide by igniting, has also been used as the starting point of a large number of atomic weight determinations. This method, which was first recommended by Norris, Fay, and Edgerly (*Am. Chem. Journ.*, 1900, xxiii., 105) is evidently closely allied to the method rejected by Brauner, viz., the oxidation of tellurium with nitric acid. While in a long series of experiments in which more than 80 grms. of substance were used, P. Koethner (*Ann. d. Chem.*, 1901, cccxix., 1) obtained exceedingly concordant results, which only varied from 127·55 to 127·66, Gutbier (*loc. cit.*) in eight experiments obtained values from 125·8—127·8. On the other hand, J. F. Norris (*Journ. Am. Chem. Soc.*, 1906, xxviii., 1675) has recently confirmed Koethner's results.

Another point must be taken into consideration in the use of the basic nitrate for atomic weight determinations. It is very sensitive to moisture, so that it can only be freed from the nitric acid mother-liquor by means of absolute alcohol.

Telluric acid was first used by Staudenmaier (*loc. cit.*) to determine the atomic weight of tellurium. He transformed the hydrate, $H_2TeO_4 + 2H_2O$ or H_6TeO_6, into tellurium oxide by igniting it. From a long series of experiments, in which altogether 22·5 grms. of substance were used, the value 127·16 was calculated. The numbers obtained lay between 127·08 and 127·27. When telluric acid was reduced to tellurium the same author in three experiments, using 4·8 grms. of substance, found the mean value 127·28. Gutbier (*Ann. d. Chem.*, 1902, cccxx., 52), using the first reaction and only 1·5 grms. of substance in two experiments, weighed the water formed in a calcium chloride tube, and not the TeO_2, and found Te = 127·65, and when telluric acid was converted into tellurium obtained the mean value 127·34 (127·00—127·80). Finally, Heberlein transformed 3 grms. of telluric acid into dioxide and weighed the latter; in two experiments he found 126·72 (126·60 and 126·84).

Besides the methods described above many others have been used for the atomic weight determinations. It is not necessary to give details of them here, because either they were described too shortly to be criticised, or else the quantities of substance used were too small.

As those methods which were carried out with the greatest exactitude were always those which give a higher atomic weight for tellurium than that of iodine, many of the above authors have endeavoured to find out whether tellurium is accompanied by an element of higher atomic weight; this assumption was first suggested by Mendeleeff, and Brauner thought he had obtained experimental confirmation of it. However, all attempts to decompose tellurium have given a negative result. Their value has lain in the fact that they have given us excellent methods of preparing pure tellurium. Koethner's method cannot be excelled for this purpose.

Mendeleeff's hypothesis also suggested the experiments I now propose to describe. Telluric acid was subjected to fractional crystallisation on a large scale by the column system, in order to test whether any differences could be observed in the different fractions. Staudenmaier (*loc. cit.*) had already separated telluric acid from its solutions in some fractions, and found that it was not complex, and F. Mylius (*Ber.*, 1901, xxxiv., 2208) had confirmed this result in the course of his complete investigation of telluric acid; but these experiments did not take sufficient account of the possibility of the existence of an isomorphous mixture, which could be split up only by a systematic crystallisation process. I therefore decomposed about 1500 grms. of telluric acid by several hundred crystallisations into twenty fractions of approximately equal size, and found not the least difference between the first and last fractions. If we remember that a similar research which Norris, Fay, and Edgerly (*loc. cit.*) had carried out with potassium tellurium bromide, K_2TeBr_6, on a somewhat smaller scale, also gave a negative result, like all other attempts to decompose tellurium by chemical methods, we can no longer entertain any doubt about its simple nature.

As by these experiments I obtained a large quantity of very pure telluric acid I decided to use it to determine the atomic weight of tellurium, under better conditions than Staudenmaier.

Preparation of the Material.

1¼ kilogrms. of raw tellurium containing more than 75 per cent of tellurium, which had been obtained from the Royal Hungarian Foundries in Selmeczbanya, was first converted into the dioxide, and roughly freed from impurities (copper, lead, silver, &c.). The dioxide was oxidised to telluric acid by chromic acid by a modification of Staudenmaier's method. For this purpose one part by weight of TeO_2 was suspended in 1¼ parts by weight of

nitric acid (sp. gr. 1·4), and the theoretical quantity of chromic acid anhydride, dissolved in five times the quantity of water, was added in small portions. The reaction evolves much heat. Finally, the solution was heated on the water-bath till it had become clear. On cooling, the greater part of the telluric acid formed crystallised out; the residue was obtained by evaporation and then by the addition of strong nitric acid. The telluric acid thus obtained was subjected directly to the above crystallisation process only because it must have been purified in the course of these operations. The last mother-liquors were always re-precipitated with nitric acid, and thus, finally, nearly 1½ kilogrms. of perfectly pure telluric acid was obtained almost without loss. It was not until no impurity except nitric acid could be detected in the last liquors, and in particular no further trace of a sulphuretted hydrogen reaction appeared, that the further crystallisations were undertaken with special precautions. Little flasks of Jena glass were used; they had previously been boiled with water and acids, and finally rinsed out with water vapour. Into these the warm fairly concentrated solutions were filtered, so that on cooling crystals formed in large quantities on the bottom. The narrow necked flasks were protected against dust by means of covers. Then the mother-liquor of each crystallisation was poured without filtration on to the following fraction, the last liquor was concentrated in platinum dishes, and then poured into a Jena flask. If the first crystallisation, which was always re-crystallised from fresh quantities of pure water, had become too small, it was added to the subsequent fraction, previously re-crystallised from pure water. The same process was repeated with the final mother-liquors, except that the last residues, in which nitric acid had accumulated, were finally put aside, by which only a few grms. of telluric acid were removed from the crystallisation process. After about twenty equal fractions had thus been obtained, the last of which was quite free from nitric acid, the material for the atomic weight determinations was separated. For this purpose the fraction chosen was brought into solution by warming with its mother-liquor, the solution was poured into a platinum dish, and allowed to cool quickly, being stirred with a platinum spatulum. The acid separated in a fine crystalline mass. This was well drained on a Nutschen filter, the bottom of which was covered with hardened filter-paper, and dried in a desiccator over sulphuric acid. The only impurity which could still remain in the material was mother-liquor and water. Hence the greatest care was taken to dry the telluric acid. Some of it was allowed to stand in a thin layer in a vacuum over phosphoric acid anhydride until its weight was constant, which was always the case after twenty-four hours, and the rest was very finely powdered and sifted through a fine-meshed gauze sieve, and then treated similarly. Of the following atomic weight determinations Nos. 1, 2, and 5 were carried out with unsifted and the others with sifted material. No difference could be detected. Finally, in one case, No. 6, the telluric acid was allowed to stand for two months in a vacuum over phosphoric acid anhydride. It might have been expected that in this case the telluric acid would have shown some loss of weight, but it did not; 15 grms. of the substance showed a loss of only 0·3 mgrm., *i.e.*, its weight was practically constant.

The Atomic Weight Determinations.

The atomic weight was determined from the telluric acid by transforming it into dioxide, according to the equation $H_6TeO_6 = TeO_2 + O + 3H_2O$. Staudenmaier had used the same reaction, and for this purpose had heated the acid in a hard glass flask, the neck of which was closed by an asbestos stopper. This method seems rather too rough for an atomic weight determination, and I therefore altered it as follows:—

A pear-shaped platinum vessel was employed for the heating, such as F. W. Hinrichsen (*Zeit. Physik. Chem.*, 1902, xxxix., 311) used in determining the atomic weight of calcium and has described fully. As counterpoise a second vessel of exactly the same shape and weight was used. Thus, not only were the reductions of the weighings to vacuo simplified, but also I was independent of errors which might be caused by the increase of weight of larger vessels during the weighing, owing to the formation of a layer of water.

The heating was performed in an electric resistance furnace, which was arranged so that the bottom could be specially heated. The platinum vessel rested on three platinum supports fastened on the bottom, and about three quarters of its height projected above the furnace through a platinum ring. The temperature of the bottom of the vessel was measured by means of a Le Chatelier element with a millivoltmeter. In the upper parts of the platinum vessel the temperature remained a good deal lower, which was necessary in order that the tellurium dioxide might not volatilise. During the experiments the temperature was very slowly raised in the course of two to three hours from 100—160°, because between these temperatures two molecules of water escape, and care had to be taken that the powdery mass did not cake together. This was always successfully avoided when the above method was adopted. Experiment 4, however, was intentionally carried out much more quickly than the others in order to find out when the acid was transformed into the dioxide rather more rapidly, the final result obtained would be nearer Staudenmaier's. The opposite was the case. Hence, in calculating the final result this experiment is excluded as obviously and purposely incorrectly performed.

Then during the next three or four hours the temperature was gradually raised to 650°, and this temperature was maintained for about an hour. The residue then always appeared perfectly white, and was thus free from TeO_3, which, when present even in the minutest quantity, always gives the dioxide a yellow colour. After weighing, the heating was repeated for an hour, sometimes increasing the temperature by 80°, and no decrease of weight was observed.

During the heating in the first four experiments the platinum vessel was kept open until the temperature had risen to 300°, so that the water vapour could escape easily. Then a well-fitting cover was placed loosely on, and taken off when the vessel was taken from the furnace. During the cooling the excess of oxygen contained in the vessel diffused into the atmosphere.

(Note.—Staudenmaier heated in a narrow necked glass flask loosely closed with asbestos. As he did not expel the oxygen by air after heating, the weight of his residue must have been a little too high).

In the last two experiments the method was altered. In order to find out whether some telluric acid volatilised with the water vapour, or some tellurium oxide with the oxygen, the cover described by Hinrichsen (*loc. cit.*) was placed on the platinum vessel, so that a current of dry air could be led through the apparatus during the heating. The escaping water vapour condensed in a platinum tube and dropped into a platinum crucible. The cover, tube, and crucible were weighed before the experiment. After the heating they were heated to 150° in a drying oven and then weighed again. No loss of weight exceeding 0·1 mgrm. was ever observed.

It need hardly be mentioned that all the necessary precautions and corrections were applied to all the weighings. Dry telluric acid is not so hygroscopic that there is any difficulty in weighing accurately in the covered platinum crucible. When allowed to stand in air it does gain considerably in weight.

First of all, a middle fraction of the different crystallisations, viz., the ninth, was used for the experiments. One part of this acid served for the preliminary experiments to perfect the method. In the following table all the results are collected which were obtained in experiments which had atomic weight deterimations for their special aim. The first experiment was performed with the ninth

fraction, the next two with the first, and the last three with the twentieth. The results showed that it was unnecessary to do more experiments. Experiment 4 was excluded for the reasons given above. In the calculation O was taken = 16, H = 1·008.

No.	Fraction.	Weight of H_6TeO_6.	Weight of TeO_2.	Loss of weight (per cent).	Te.	Deviation from mean.
1.	IX.	8·6277	5·9884	30·591	126·93	+0·08
2.	I.	12·2680	8·5135	30·604	126·84	±0·01
3.	I.	13·0051	9·0244	30·609	126·80	- 0·05
4.	XX.	8·6415	5·9947	30·629	126·65	—
5.	XX.	8·4588	5·8696	30·6095	126·80	- 0·05
6.	XX.	8·0113	5·5399	30·591	126·94	+0·09
		50·3699	34·9558	30·602	126·85	

The experiments thus led to the unexpected result that the atomic weight of tellurium is—

$$126{\cdot}85 \pm 0{\cdot}02 \text{ (probable error)},$$

thus lower than that of iodine (I = 126·97), and 0·75 units (0·6 per cent) lower than the value given by the International Commission.

It is very improbable that my method could be affected by so large an error. The purity of the material is guaranteed by the agreement in the values obtained with the first and last fractions. It can hardly be supposed that a constant amount of moisture caused the greater loss on ignition, since the result remained the same, whether the telluric acid was left *in vacuo* over phosphoric anhydride either in a coarse mass for one day or in a fine powder for two months. It is equally unlikely that in the experiments described the greater loss on ignition was due to the volatilisation of a tellurium compound. Other sources of error which might give too low a value seem to be absent.

As may be seen from the figures given at the beginning of this article, other workers have found an atomic weight of tellurium differing but little from the value obtained by me. Allusion need only be made to the researches of Staudenmaier and Heberlein. Other facts in the chemistry of tellurium seem to confirm the lower atomic weight. O. Steiner (*Ber.*, 1901, xxxiv., 570) determined in a series of analyses the carbon contained in very carefully purified diphenyl telluride, and calculated from it the atomic weight of tellurium. The results lie between 126·1 and 126·7, while two control experiments with diphenyl selenide gave for Se 78·8 and 79·3 instead of 79·2. In his article the author rightly states that his numbers, even if they have not the importance of trustworthy atomic weight determinations, nevertheless argue against an atomic weight of over 127 for tellurium.

The results which B. Brauner (*Monatsh. fur Chem.*, 1890, xi., 526; 1891, xii., 29), and Gooch and Peters (*Zeit. Anorg. Chem.*, 1899, xxi., 405) obtained in the determination of tellurium dioxide, are very noteworthy. The first-named carried out a very thorough investigation of the subject, and found that all the methods he tested gave too high a value. These methods, which proved to be the best, gave in a long series of experiments 0·20—0·47 per cent, or on an average 0·35 per cent too much. If the value found by me for the atomic weight of tellurium is used in the calculation, Brauner's deviations are −0·27 to ± 0·00 per cent, or an average of −0·12 per cent. Gooch and Peters at the end of their article state that the average found by them would agree with the theory if tellurium was taken to be 127 instead of 127·5, the value employed in their calculation. The atomic weight of tellurium must now be checked by a titration method.

The cost of this research was defrayed by means put at my disposal in 1905 by the Jagor Fund. The unpleasant physiological effects due to working with tellurium (*cf.* Mylius, *loc. cit.*) have considerably delayed the investigation.—*Berichte*, 1907, xl., 4730).

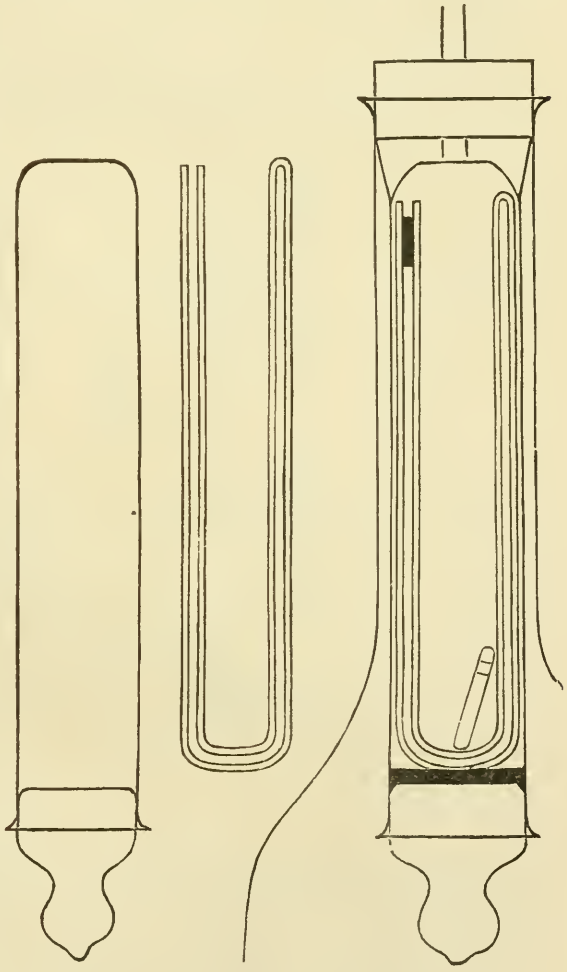
A NEW METHOD SUGGESTED FOR DETERMINING VAPOUR DENSITIES.

(SECOND COMMUNICATION).

By PHILIP BLACKMAN.

THE apparatus described by the author in the CHEMICAL NEWS, 1907, vol. xcvi., p. 223, may be simplified as here detailed.

The apparatus consists of a long vessel with an air-tight stopper. The manometer is a U-capillary tube, with one end closed, and of a size that it fits conveniently into the vessel; it has a scale of cm. (divided into tenths and



numbered) marked right round it facing outwards, so that when it is fixed in the vessel the readings can be easily observed from the outside.

The open end of the U-tube is placed in mercury, the other end warmed and then cooled, and a thread of mercury thus introduced. The U-tube is placed in the vessel, some mercury (5 cc.) poured in to help to seal the stopper, the weighed substance introduced, the stopper fixed and wired on, and the whole heated.

It would perhaps be more advantageous to have the U-capillary tube open at both ends; two threads of mercury would in this case have to be introduced, one at each end.

MELTING-POINTS OF THE IRON GROUP ELEMENTS BY A NEW RADIATION METHOD.*

By G. K. BURGESS, Associate Physicist, Bureau of Standards.

Recently Dr. Waidner and the author suggested two radiation methods for the determination of high melting-points of substances in minute quantities ("On the Determination of Melting-points by Radiation Method," *Phys. Rev.*, 1906, xxii., 359). The first depends on the total radiation from a surface as measured in terms of some instrument making use of the Stefan-Bolzmann law. The second method is based on the measurement of the intensity of a particular monochromatic radiation from platinum or other substance; that is, it makes use of an instrument based on Wien's equation. (A discussion of the laws of radiation will be found in *Bulletin*, Bureau of Standards, 1905, i., 189.)

Some preliminary measurements made at that time by the second method on the metals of the iron group showed it to possess considerable accuracy and to be particularly applicable to the easily oxidised elements if the melts were obtained in an atmosphere of pure hydrogen It was also demonstrated that a compound of one of the refractory elements, which could be reduced to the metal by hydrogen, might serve as material for determining the melting-point of the pure metal.

The present paper is an account of the application of this second method to the determination of the melting-points in hydrogen of the members of the iron group, using, for the measurement of temperature a Holborn-Kurlbaum optical pyrometer, and the data on the monochromatic radiation from platinum published by Waidner and Burgess in *Bulletin*, Bureau of Standards, 1907, iii., 1.

Experimental Method.—The arrangement of the apparatus is shown in Fig. 1, and is as follows:—Within the blackened brass cylinder C is a strip of pure platinum P, about 6 cm. long, 4 mm. wide, and 0·02 mm. thick. This platinum strip is heated electrically to any desired temperature, and by means of a rheostat, which has a fine adjustment, very delicate control of the temperature of P is obtained. The cylinder C is connected to an electrolytic hydrogen generator in series with an alkaline pyrogallate solution and a drying tube of calcium chloride. At M is a removable window of thin mica, giving access to the cylinder and permitting observation of P both with the microscope N and the optical pyrometer H.

To take an observation of a melting-point, a minute quantity of a metal or its oxide, usually about 0·001 mgrm. in the form of powder, is placed at the centre of the platinum strip P, the window M screwed down, the cylinder closed and filled with hydrogen, and then the electric circuit is made through P. One observer watches the metallic speck or dust through the microscope and gradually increases the current until the melting-point is reached, while, simultaneously, another observer reads this temperature with the pyrometer. Only one melt is taken on a given platinum strip.

Temperature Scale.—The Holborn-Kurlbaum pyrometer was calibrated by sighting upon an improved form of the electrically heated experimental black-body due to Lummer and Kurlbaum, the temperature of which was given by the electromotive forces of two platinum, platinum-rhodium thermoelements as measured on a potentiometer. The temperature scale of the thermoelements was obtained by assuming the following melting-points: Zn = 419·0° C., Sb = 630·5°, Cu = 1084·0°, all these metals being of "Kahlbaum" purity. As an upper fixed point, the melting-point of platinum was taken as 1753° C., determined from measurements with the optical pyrometer. In the optical pyrometer two lamps were used which gave practically identical values for every temperature observed. As the establishment of the high temperature scale of the Bureau of Standards is treated at length elsewhere in this Bulletin, further discussion of this scale need not be given here (Waidner and Burgess, *Bulletin*, Bureau of Standards, 1907, iii., 1).

The indications of the optical pyrometer, when sighted upon platinum through a mica window, are subject to two corrections, one for the reflection and absorption of the

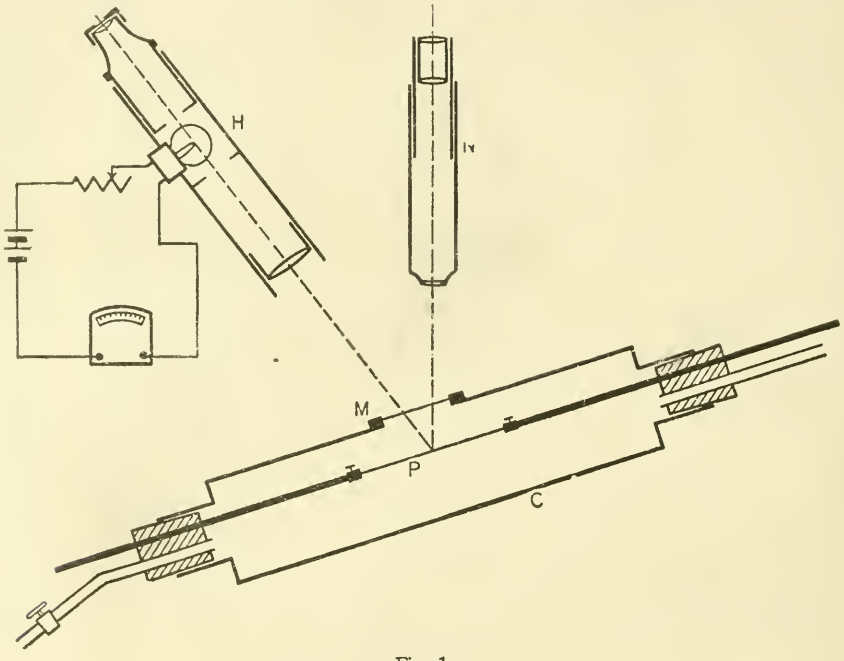


Fig. 1.

* From *Bulletin* of the Bureau of Standards, vol. iii., No. 3.

mica, the other for the selective emission of the platinum for the light used—in this case, red light $\lambda = 0{\cdot}66\mu$. The former correction, which is about 15°, is easily determined and checked between measurements of the melting-points by taking observations of the platinum brightness at a definite temperature both with and without the mica interposed, with a second mica strip always in place to prevent air currents.

The correction for the selective emission of platinum is discussed in the paper above cited. The magnitude of this correction varies from 110 to 160° C. and is known to at least 10° within the temperature range here used.

Sources of the Materials.—Chemically pure elements are difficult to get, and it is desirable to use products from different sources and of known analyses. These experiments were greatly facilitated by the willingness of scientists possessing very pure samples to put them at our disposal.

H. Copaux, of Paris, who has recently completed a most comprehensive study of the properties of cobalt and nickel, and produced these metals containing less than 1/2000 part impurities, furnished samples of these elements ("Recherches Expérimentales sur le Cobalt et sur le Nickel," *Ann. Chim. Phys.*, 1905, vi., 508). Dr. H. Goldschmidt, of Essen Ruhr, Germany, sent pieces of his pure aluminothermic metals, namely, chromium and manganese, all of an average purity of 98 to 99 per cent; and Prof. C. F. Burgess, of the University of Wisconsin, supplied samples of his pure electrolytic iron. The other samples were from Kahlbaum and of "Kahlbaum" grade except as otherwise noted.

Iron.

Iron from two sources was used, "Kahlbaum" iron in the form of powder, and electrolytic iron in lumps, from Prof. C. F. Burgess, from which particles weighing slightly more than 0·001 mgrm. were chipped. This electrolytic iron had the following composition, as determined from an analysis of a similar sample by Mr. A. A. Blair, of Wisconsin:—

Sulphur	None.
Silicon	0·013 per cent
Phosphorus	0·004 ,,
Manganese	None.
Carbon	0·012 ,,
Hydrogen	0·072 ,,

Iron as it approaches the melting-point becomes plastic, so that the actual temperature of melting is not sharply defined, there being a considerable transition region.

The very considerable variation in the separate melts appears to be due mainly to the influence of size and shape of the particles on the viscosity and surface tension; also lack of homogeneity in chemical constitution of such minute samples may play some *role*, as well as variations in the temperature of adjacent areas of the platinum strip. That the electrolytic iron melts at a slightly higher temperature seems probable. Any impurity likely to be formed in iron will lower its melting or freezing point; but the total impurities in the electrolytic iron here used will not cause a lowering as great as 5° C.

The corrected values found for all the separate melts are given in Table I.

TABLE I.—*Melting-point of Iron.*

C. F. Burgess (electrolytic).	"Kahlbaum" (powder).
1493°	1509°
1519	1494
1518	1512
1512	1483
1512	1507
1514	1491
1489	
1508	
1508	
1494	
Means.. 1507	1499

Among previous determinations of the melting-point of iron have been the following:—

Roberts-Austen, 1899 ..	1600°
Le Chatelier, 1901	1575°
Osmond	1550°
Tammann, 1904	1555° (1490°)

The value given by Tammann, 1555° (Guertler and Tammann, *Zeit. Anorg. Chem.*, 1905, xlv., 205), is that, assuming the nickel point to be 1484°, as determined by Holborn and Wien (*Wied. Ann.*, 1895, lvi., 360). Tammann's value as obtained by extrapolation of his own thermocouple calibration from the gold point (= 1064°) would be about 1490°.

Cobalt.

Three kinds of cobalt were used; chips from M. Copaux's sample, "Kahlbaum" cobalt, and the metal obtained from Kahlbaum's nickel-free cobalt-carbonate transformed to cobalt-oxide by heating in air, and reduced to metallic cobalt by hydrogen, in place on the platinum strip on which the melt was taken.

In great contrast to iron, cobalt possesses a very sharp melting-point, and the resulting precision is correspondingly increased, showing that the greater deviations in the measurements on iron are not due to the fault of the method nor to its lack of sensitiveness.

TABLE II.—*Melting-point of Cobalt.*

	Co from $CoCO_3$. (Kahlbaum Ni-frei).	"Kahlbaum." Powder.	Copaux pieces from crucible melt.
	1456°	1470°	1457°
	1472	1466	1468
	1467	1468	1463
	1468	1466	1466
	1453	1459	1462
	1470	1461	
Means	1464	1465	1463

Copaux himself gets 1530° for the cobalt point by interpolation between the gold and platinum points, assuming the latter to be 1780°. Recent measurements of the platinum point show 1780° to be high by about 70° on the thermocouple scale, or by about 30° on the optical scale, as usually defined in terms of Wien's law. (Harker, CHEM. NEWS., 1905, xci., 62; Holborn and Henning, *Sitzber. Berlin Akad.*, 1905, xii., 311; Nernst, *Berichte Deut. Phys. Ges.*, 1906, iv., 48; Waidner and Burgess, *loc. cit.*) Holborn and Valentiner (*Ann. der Physik.*, 1907, xxii., 1), however, have recently obtained 1789° for the melting-point of platinum, using Wien's equation, the constants of which were newly determined by comparison with the indications of a gas thermometer up to 1600°. Guertler and Tammann get 1505° for cobalt on the Holborn and Wien scale, or reduced, as explained in the case of iron, their value for cobalt would be about 1455° on the thermoelectric scale.

Nickel is usually present in cobalt to at least 2 per cent, causing a proportional lowering of the freezing point of less than 1° C. (Guertler and Tammann, *Zeit. Anorg. Chem.*, 1904, xlii., 353). Iron, even if present in considerable quantities, has a negligible effect on the cobalt melting-point. Cobalt is less oxidised in the air at high temperatures than are the other elements of the iron group, and cobalt oxide is only slightly soluble in the metal (Copaux, *loc. cit.*). These properties, taken together with its very sharp melting-point, the insignificant effect of its usual impurities on this temperature, and its relative cheapness as compared with the platinum metals, make cobalt, even of a commercial purity, a desirable metal to use for a fixed point in pyrometric measurements.

Nickel.

The melting-point of nickel was determined with the pure metallic nickel of M. Copaux and with Kahlbaum's cobalt-free nickel oxide reduced by hydrogen on the

platinum strip. The melting-point is about as well defined as that of cobalt.

Table III.—*Melting-point of Nickel.*

Pressed nickel (Copaux).	Ni from the oxide (Kahlbaum).
1434°	1433°
1435	1431
1434	1439
1436	1434
1436	
Means.. 1435	1435

The preliminary measurements of Dr. Waidner and the author showed that "Kahlbaum" nickel also gave the same value as the above.

The following thermoelectric determinations of the nickel point may be noted :—

Le Chatelier, 1887.. ..	1420°
Holborn and Wien, 1895	1484°
Harker, 1905	1427°
Tammann, 1905	(1425—1430°)
Copaux, 1905	1470°

The measurements of Copaux and of Holborn and Wien are subject to the same corrections as discussed under cobalt. Le Chatelier's determination is based on a too low value of the gold point. Tammann's value is that deduced from his own observations as in the case of cobalt and iron. According to the measurements of Waidner and Burgess (*loc. cit.*) the optical is 8° higher than the usual thermoelectrie scale at 1427°, so that the nickel freezing point, as determined by Harker using thermocouples, is in exact agreement with the above optical determination.

The presence of cobalt in nickel as impurity will raise the melting-point, while iron as an impurity in nickel will lower its melting-point (Tammann, *loc. cit.*).

Chromium.

Crystallised chromium from Kahlbaum was used and also Dr. Goldschmidt's aluminothermic chromium of 98—99 per cent purity and carbon free. As Table IV. shows, it is about as difficult with chromium as with iron to get a sharp melt. Possibly the greater impurity of the crystallised chromium increases this effect for that sample.

Table IV.—*Melting-point of Chromium.*

Chromium crys. Kahlbaum.	Chromium, 98—99 per cent. Goldschmidt.
1501°	1497°
1472	1483
1480	1486
1505	1484
1475	1494
Means.. 1487	1489

A thermoelectric determination of the chromium melting-point has been made by E. A. Lewis (Chem. News, 1902, lxxxvi., 13), using 99 per cent chromium obtained by the Goldschmidt process. The melt was made in a lime crucible in an oxy-coal-gas flame ; two melts gave 1510° and 1520°.

Manganese.

Two samples of manganese were used : "Kahlbaum" manganese, and a sample from Dr. Goldschmidt, 98 per cent manganese, carbon free and technically iron free. The manganese point, although the lowest in the series, is the least satisfactory to determine on account of the very great temperature interval (over 25° C.) in which the melt takes place.

First signs of melting were evident as low as 1195° C., and the melt of relatively large pieces was not complete at 1220° C.

Table V.—*Melting-point of Manganese.*

Manganese. "Kahlbaum."	Mn. 98 per cent. Goldschmidt.
1226°	1207°
1203	1210
1197	
1198	
Mean. .. 1207	

Heraeus found 1245° (*Zeit. Elec. Chem.*, 1902, viii., 185), by observing with a telescope the melt in hydrogen within an electric furnace, whose temperature was given with a thermoelement and pyrometer-galvanometer. Levin and Tammann, also using a thermo-element, get between 1190° and 1200° for the manganese melting-point (*Zeit. Anorg. Chem.*, 1905, xlvii., 136).

Conclusion.

The values found by the radiation method described above, for the melting-points, in an atmosphere of hydrogen of the elements of the iron group in contact with platinum, are as follows :—

Table VI.—*Approximate Melting-points of the Iron Group.*

Metal.	Melting-point.	Purity.
Iron..	1505° C.	99·95
Chromium ..	1489	98—99
Cobalt	1464	99·95
Nickel	1435	99·95
Manganese ..	1207	98—99

Of these, the cobalt and nickel melting-points appear to be correct to within 5°, while the uncertainty of the iron, chromium, and manganese points is probably less than 10° C. It is not probable that any of these metals combines with platinum, or alloys with it until the metal is melted at its natural melting-point. The fresh melts are all white, changing to the colour characteristic of each metal after standing in the air.

It is not claimed that the above numerical values are final, and they are given mainly as an illustration of the possibilities of a method which may be the only one available in certain cases. The above values are, however, in excellent agreement with certain of the latest determinations by the thermoelectric method, notably Harker's determination of the nickel-point, and the determinations of Tammann and his associates for iron, nickel, cobalt, and manganese, when these latter results are reduced by extrapolation from the gold point and account is taken of the difference between the thermoelectric and optical scales (Waidner and Burgess, *Bulletin*, Bureau of Standards, 1907, iii., 1). It would be highly desirable to determine the melting-point of cobalt with the greatest accuracy for use as a fixed point in pyrometry.

By this radiation method less than 0·001 mgrm. is required for a single observation, making it readily applicable for the relatively exact determination of the melting-points of the rarer refractory elements, and it is the only sensitive method yet suggested when the pure element can be obtained only in very small quantities. It is our intention to continue such determinations whenever it is possible to obtain the refractory elements of sufficient purity.

There may be considerable variations in size of the particles to be melted without appreciable change in the apparent melting-point. Furthermore, the method gives the same melting-point for the pure metal, and for the metal reduced from the pure oxide by hydrogen in the apparatus used, and requires no transfer or handling of the microscopic quantity of the metal so formed.

For the determination of the melting-points of those elements having a higher fusing point than platinum, iridium strips may be used and in some cases perhaps carbon ; but it is hoped that we may shortly be able to use tungsten strips. Tungsten, as we have found (Waidner and Burgess, "Temperature and Selective Radiation of Incandescent Lamps, *Electrical World*, Nov. 10, 1906,

915; *Bulletin*, Bureau of Standards, 1906, ii., 319), appears to have the highest melting-point—above 3000° C.—of any element that can be melted without considerable previous evaporation, and appears to possess the further advantage of being unattacked by hydrogen. The above apparatus could evidently be arranged, if necessary, to work with a vacuum instead of an atmosphere of hydrogen or other gas.

It might also be possible, as in the case of steels, to apply the method to a determination of carbon or other content from the melting-point measurements.

To Mr. J. R. Fehr credit is due for efficient aid in carrying out the above experiments.

THE DETERMINATION OF SILICA AND ALUMINA IN IRON ORES.

By G. W. DEAN.

Further experience with the method which was described in the *Journal of the American Chemical Society*, vol. xxviii., 882, has led to its modification in two or three important particulars. It has been found that the ore may be ignited directly instead of separating and igniting the residue from digestion with hydrochloric acid. It has also been found that a porcelain crucible is the most suitable for the ignition, since the ore is less liable to be overheated and the alumina rendered insoluble. When the determination of alumina is not required, the use of stannous chloride aids greatly in dissolving the ore. It has also been found that by heating the ore with sulphur it is partly reduced in such a manner that it is more easily soluble in hydrochloric acid and the whole method can be used when it is desired to determine both silica and alumina. The methods which are now used are as follows:—

Determination of Silica alone.—Weigh 0·5 grm. of the finely pulverised ore (100 mesh), transfer to a 20 cc. porcelain crucible, cover and heat over a Dangler burner until the contents of the crucible are dull red, raise the temperature for a few seconds and then remove the crucible from the source of the heat. The whole operation should take not more than two or three minutes. Transfer the ignited ore when cold to a beaker, add 20 cc. strong hydrochloric acid containing 1 grm. of stannous chloride in 225 cc. Boil vigorously until solution is apparently complete, and for five or ten minutes longer. Twenty or thirty minutes will usually be enough. If the ore is very difficult to dissolve, a stronger solution of stannous chloride or more of the same solution may be used. Dilute slightly, filter, and wash thoroughly first with dilute hydrochloric acid and then with water. Ignite and weigh the silica as usual.

2. *Determination of both Silica and Alumina.*—Weigh 0·5 grm. of the finely pulverised ore (100 mesh), transfer to a 20 cc. porcelain crucible, and place on top 0·25 to 0·40 grm. of sulphur; heat gradually until the ore is dull red and then raise the temperature slightly for ten seconds. Transfer to a beaker, pulverise the mass with a glass rod, add 25 cc. of hydrochloric acid, and boil vigorously for fifteen minutes. Then add enough nitric acid to clear the solution and decompose the sulphides and boil vigorously for another five or ten minutes, repeating the addition of nitric acid and boiling if required. If dark particles remain undissolved after this treatment, it is probable that further treatment will not decompose them. Dilute, filter, wash, and determine the silica, as before, and in the filtrate determine the alumina by any one of the various methods which are suitable. In this method the ignited mass is treated with hydrochloric acid, first to gain the advantage of the reducing action of the hydrogen sulphide liberated from the sulphide of iron formed by the action of the sulphur. If the nitric acid is added at first, the advantage of this reducing action is lost, and the oxides of iron are often very difficult to dissolve.

The methods have been applied to the determination of silica in the following ores:—(1) Arizona hematite; (2) Wyoming low grade hematite; (3) Alabama limonite; (4) Alabama hematite; (5) Magnanite from Llano County, Texas; (6) Michigan magnetite; (7) Michigan hematite; (8) Mesabi limonite; (9) Mesabi decomposed hematite; (10) Swedish hematite; (11) Swedish magnetite; (12) Highly aluminiferous hematite from Baraboo iron district; (13) Hematite from Port Arthur field in Canada; (14) Bog iron from Nova Scotia. The results are as follows (Determinations are in duplicate):—

	Per cent silica by Na_2CO_3 fusion.	Per cent silica by hydrofluoric acid method.	Per cent silica by above method.
1.	12·06—12·20	12·08—12·10	12·09—12·13
2.	21·27—21·22	21·11—21·20	21·26—21·23
3.	13·77—13·68	13·69—13·72	13·73—13·62
4.	11·99—11·82	11·88—11·94	11·92—11·83
5.	14·28—14·33	14·32—14·31	14·36—14·41
6.	9·91— 9·99	9·82— 9·89	9·80— 9·81
7.	10·55—10·40	10·49— —	10·50—10·52
8.	8·02— 8·00	8·15— 8·10	7·99— 8·08
9.	17·82—17·74	17·85—17·77	17·86—17·88
10.	7·09— 7·13	7·00— 7·04	7·06— 7·01
11.	6·72— 6·84	6·72— 6·67	6·74— 6·77
12.	31·12—31·18	31·09—31·12	31·08—31·11
13.	4·44— 4·52	4·40— 4·52	4·38— 4·40
14.	2·06— 2·05	2·08— 2·03	2·09— 2·00

It is evident from the above that the method gives accurate results when applied to a great variety of ores.—*Journal of the American Chemical Society*, xxix, No. 8.

THE CORROSION OF IRON AND STEEL.

By WILLIAM H. WALKER, ANNA M. CEDERHOLM, and LEAVITT N. BENT.

Some time ago an investigation was undertaken in the Research Laboratory of Technical Chemistry of the Massachusetts Institute with a view to throwing some light upon the much discussed question as to whether wrought iron is more resistant to corrosion than is steel. To this end a relatively large quantity of pure iron was prepared, and with this as a basis, alloys of iron and varying amounts of the different elements occurring in commercial iron and steel were made by melting the constituents in alumina crucibles heated by an electric furnace operating under a high vacuum. In studying the specimens so produced, it early became apparent that a more complete understanding of the factors which occasion corrosion and the conditions under which corrosion proceeds was necessary in order that our results could be intelligently interpreted. A study of the literature on the subject showed it to be so voluminous and so altogether contradictory, that as a first step in our investigation of the general subject of the influence of the constituents of iron or steel upon its corrosion, we decided to determine, if possible, the mechanism of the reactions by reason of which corrosion takes place.

(Since this part of the work was undertaken we have learned that Dr. Allerton S. Cushman, Assistant Director, Office of Public Roads, Washington, has also been investigating this subject. Although contemporaneous, the investigations have been carried on entirely independently, except in regard to the ferroxyl indicator, and it is believed that Dr. Cushman's work will be found to confirm in many respects the results herein recorded.

Theories of Corrosion.

The more important theories of the corrosion of iron and steel which seem to be worthy of discussion may be considered under three heads, the first, when taken up chrono-

* Read before the New York Section of the American Chemical Society, May, 1907. From the *Journal of the American Chemical Society*, xxix., No. 9.

logically, being the *carbon dioxide theory*. Although the subject of corrosion had been investigated by a number of workers, Dr. Crace Calvert in 1871 seems to have been the first to have carried on a systematic study of the factors entering into the reaction, and concludes that at least three reagents are essential, viz., water, oxygen, and carbon dioxide. This work received a complete endorsement at the hands of Crum Brown in 1888, who summarised the successive changes in the process of corrosion in the following equations :—

$$4(Fe + H_2O + CO_2) = 4FeCO_3 + 4H_2.$$
$$4FeCO_3 + 6H_2O + O_2 = 2Fe_2(OH)_6 + 4CO_2.$$

Two important facts regarding corrosion may be so easily explained by this theory that it has been very generally accepted by text-book writers and thus gained credence. These facts are, first, that the presence of carbon dioxide accelerates corrosion, and, second, that alkalis such as calcium hydroxide entirely prevent corrosion.

The latest and possibly most convincing work to be done on this subject is that of Gerald T. Moody, which apparently proves that no corrosion of iron will take place without carbon dioxide (*Journ. Chem. Soc.*, lxxxix., 720).

Moody's principal experiment consisted in exposing a bright piece of pure iron immersed in water to a stream of oxygen, the utmost precautions having been taken to exclude the presence of carbon dioxide. The different parts of the apparatus were connected by glass seals, and in order to free them from carbon dioxide, air, after passing through a most elaborate washing and purifying system, was drawn for three weeks through the apparatus. Notwithstanding these precautions, rust in small amounts was found to develope on the specimens after a few days. When, however, air from which the carbon dioxide had not been absorbed was drawn through the water in which the iron was immersed, corrosion rapidly increased.

Moody concluded that the very small amount of rust which he had observed before the unwashed air was led in, was due to a trace of carbon dioxide which had been introduced with the piece of iron. He therefore immersed his specimens in a 1 per cent solution of chromic acid in order that they might be protected from the carbon dioxide until the apparatus had been swept entirely free from this gas. After again drawing carbon dioxide-free air through the system for three weeks, the chromic acid was displaced by passing through the tube containing the iron a large quantity of pure water, introduced in such a manner as to insure no contamination with carbon dioxide. This water entirely removed all traces of this protective chromic acid solution. Carbon dioxide-free air was then drawn through the water and over the iron for five weeks, and at the end of that period no rust could be observed. The connection between the washing system and the specimen was then broken and unwashed air drawn through the water. Very considerable corrosion was observed after three days.

Electrolytic Theory.—In 1903, W. R. Whitney (*Journ. Am. Chem. Soc.*, xxv., 394) published the results of an investigation, which furnished data on which he based a theory of corrosion in accordance with the conceptions of Nernst and the modern theory of solutions. In accordance with this theory metals can dissolve only by entering the solution as electrically charged ions. This escaping tendency of a metal is measured by a force known as the electrolytic solution pressure, which will operate in any solution until counterbalanced by the osmotic pressure of the metal already in solution. In passing into the ionised state, the ions assume their positive charges while the residual negative charges remain upon the metal. Action is therefore immediately arrested on account of the difference of potential which would exist between the positively charged ions and negatively charged metal. In the case when iron is immersed in a solution of copper sulphate, there are present the positively charged copper ions which have a smaller solution pressure than the positively charged iron ions, and hence when the former are attracted to the negatively charged metallic iron their charges are neutralised and metallic copper is precipitated. Since its solution pressure is less than that of the iron, there is little tendency for the copper ions to again dissolve in the presence of iron, and the action continues.

Hydrogen acts as a metal and has an electrolytic solution pressure which places it between iron and copper in the series of metals. Iron placed in a solution containing hydrogen ions will therefore dissolve at a velocity dependent in general upon the concentration of the hydrogen ions and the ease with which the gas can be liberated upon the iron surface. Water is dissociated to a small extent into hydrogen and hydroxyl ions, and hence, if this theory holds, iron should pass into solution to a slight extent, with the liberation of an equivalent amount of hydrogen. Any reagent which increases the concentration of the hydrogen ions, such as an acid, will increase the corrosive action, while any agent which will decrease this hydrogen concentration will inhibit corrosion. In this way is explained the protecting effect of the alkalis and of any substance, for example, borax, which by hydrolysis yields hydroxyl ions, inasmuch as the product of the hydrogen and hydroxyl ions must remain a constant. The formation of rust is thus seen to be a secondary action, brought about by the oxidation of the already dissolved iron by the action of atmospheric oxygen. The role of carbon dioxide is but that of any acid, increasing by its presence the concentration of the hydrogen ions and to this extent accelerating the action.

Hydrogen Peroxide Theory.—Dunstan, Jowett, and Goulding (*Journ. Chem. Soc.*, 1905, lxxxiv., 1584) repeated the work of Whitney and failed to get any evidence that iron dissolved in pure water free from oxygen and carbon dioxide. They therefore considered this theory untenable, and advanced a theory based upon the fact that when some metals oxidise in water, hydrogen peroxide is frequently formed. The chemical action taking place when iron corrodes in water with access of oxygen is represented by these authors as follows :—

$$Fe + H_2O = FeO + H_2.$$
$$H_2 + O_2 = H_2O_2.$$
$$2FeO + H_2O_2 = Fe_2O_2(OH)_2 \text{ (rust)}.$$

Although a great deal of experimental work was done, these investigators failed in every instance to get evidence of the presence of hydrogen peroxide in the oxidation of iron. This theory explains the fact that when zinc corrodes in water hydrogen peroxide may be detected, by the supposition that hydrogen peroxide can exist upon the surface of zinc, while when iron corrodes the hydrogen peroxide is incapable of existence on the surface of the iron long enough to make detection possible. Support for this idea is found in the fact that, in every case, those reagents which inhibit rusting are also substances which decompose hydrogen peroxide.

Experimental.

Evidently the first question to be settled is—Is carbon dioxide essential to corrosion? To this end we repeated the experiments of Moody, duplicating his apparatus and method in every possible particular. In general, our observations coincide with his. Our explanation of the phenomena observed, however, differs radically from his. It is well known that pure water attacks with considerable ease all glass except that which has been most carefully prepared, producing an alkaline solution. It is also well established that in pure water a relatively small amount of free alkali will inhibit rusting. We therefore again repeated Moody's experiment, but constructed the apparatus so that a little phenolphthalein could be introduced after the water had been passed through the tube containing the iron. Both the water which was on the iron and also that which had passed over the iron into a flask beyond showed a distinct bright red when the indicator was added. When air containing carbon dioxide was passed through the solution this alkali was converted into the acid carbonate and the corrosion accelerated. When Jena glass which had been steamed for two days was employed, the

iron corroded almost as readily as when left in the open air. We feel satisfied that in our experiments (and we believe the same to be true of Moody's) the tardy corrosion of the iron was due to the inhibiting effect of the free alkali present, and that iron does rust in the presence of air containing no carbon dioxide.

All those experiments of Moody in which chromic acid was used are rendered worthless, so far as showing the preservation of iron in the absence of carbon dioxide is concerned, by the fact, apparently overlooked by Moody, that immersing iron in chromic acid or potassium dichromate will render it relatively passive. We have repeated these experiments a number of times, carrying on simultaneously a check experiment in which we treated a specimen of the same iron with a portion of the same chromic acid solution, but drew ordinary unwashed air through the apparatus. No difference could be observed in the latter case. The fact that iron is preserved by solutions of the chromates was mentioned by Wood in 1894 (*Trans. Am. Soc. Mech. Eng.*, xvi., 384), and later by a number of writers including Moody himself. No one seems to have noticed, however, that the passivity imparted to iron by such a solution is retained by the specimen after it is washed with pure water and dried. Without going further into this phenomenon we can but give it as our opinion that the apparent non-corrosion of iron in the absence of carbon dioxide is due, not to the fact that no carbon dioxide is present, but to the fact that the iron is protected by the as yet not clearly understood condition of passivity, brought about by its immersion in a chromic acid solution. (Since the above was written, a short notice of an article by Wyndham R. Dunstan appeared in *Journ. Chem. Soc.*, xxii., 63, in which the experiments of Moody without chromic acid have been repeated. Dunstan confirms his previous results and those stated above, in that iron rusts freely in the presence of oxygen and water containing no carbon dioxide). A further proof that carbon dioxide is not essential to corrosion will be given later under the consideration of the influence of oxygen on corrosion.

The failure of the writers already noted to duplicate the results of Whitney, probably accounts for the fact that the electrolytic theory has not been more generally accepted. Even so valuable a text-book as "General Inorganic Chemistry," by Alexander Smith, does not mention the possibility of this explanation, although it makes very general use of the newer theories of chemistry involved in Whitney's work. The carbon dioxide theory and the peroxide theory of Dunstan are given sufficient space, while the electrolytic theory is ignored.

Evidently the theory of Whitney must stand or fall with the truthfulness of his statement that iron dissolves in pure water entirely feee from oxygen and carbon dioxide. Although we employed a number of types of apparatus in studying this question, the following is both very simple and satisfactory. A round bottom Jena flask of about one litre capacity is inverted on a nozzle supplying live steam, for at least twenty-four hours. This insures the removal of any easily soluble alkalis, which would otherwise destroy the neutrality of the liquid. The flask is fitted with a carefully cleaned rubber stopper through which extends a glass tube drawn down to a moderate-sized capillary at its upper end. The flask is three-fourths filled with ordinary distilled water (not conductivity water) which has previously been boiled for several hours in a block-tin heater. The water in the flask is boiled for about ten minutes, and while steam is still rapidly passing out of the opening, the stopper is removed and a piece of bright iron introduced. The stopper is again inserted, the boiling continued for another ten minutes, and while boiling the capillary is sealed. The flask is allowed to cool after thickly coating the stopper with molten paraffin. If this experiment be carefully performed, no action will be observed, the iron remaining bright and the water clear even after standing several days. When the stopper is removed and the water concentrated in a platinum dish, using every precaution to prevent contamination from dust, a strong test for iron can always be obtained by the addition of a drop of ferrocyanide or sulphocyanate of potassium solution.

Thinking that possibly enough gas had been occluded in the iron to effect the reaction, the above experiment was repeated a number of times under conditions which allowed of introducing pieces of iron which had been heated to low redness and cooled in hydrogen. In every case the presence of iron was easily detected when the content of the flask was evaporated to a few drops.

This experiment was again repeated with the additional precaution of using water which had been allowed to stand for a number of days over a large quantity of spongy metallic iron, the water being introduced into the reaction flask by distilling it from the iron in an atmosphere of hydrogen. Notwithstanding all these precautions, a distinct test for iron was obtained after the water had been concentrated. In all these experiments "blanks" were run which in no case showed that sufficient iron had been dissolved either from the glass or from the platinum to furnish the test which was obtained.

We therefore support Whitney in his statement that iron will dissolve in water which contains not more than a trace of electrolyte, no oxygen, and only that amount of carbon dioxide which is not retained by a strong alkaline hydroxide. In explanation of the failure of the investigators previously cited to detect dissolved iron, we would state that usually it is not possible to obtain an indication of iron with potassium ferricyanide; for example, in the water as it comes from the flask; concentration is generally necessary.

(To be continued).

A STANDARD OF RADIO-ACTIVITY.

In the early part of 1906 the Röntgen Society appointed a Standards' Committee to systematise as far as possible the various methods already in use for determining the dosage of X-rays, and, if possible, to establish a unit for the measurement of radio-activity. The work has been carried out largely in the laboratories of Lord Blythswood and Mr. C. E. S. Phillips. In the former the properties of X-rays bearing on the problem have been investigated, and in the latter an effort has been made to obtain a radio-active standard. The Committee have been in touch with the Intensitats Commission of the Berlin Röntgen Society, as well as with similar societies in London and on the Continent.

At the last meeting of the Society on January 2nd an interim report was presented. The Committee laid it down that the conditions essential to a radio-active standard were constancy and homogeneity. The study of the transformation products of radium showed that the Alpha and Beta rays changed with time, but that, on account of the Gamma rays all being emitted by radium C, that radiation might for all practical purposes be regarded as constant. The Gamma rays from radium are also believed to be nearly homogeneous, and therefore the Committee thought that this form of radiation appeared to fulfil the conditions essential to a standard, and that it was only necessary to eliminate the Alpha and Beta rays by passing the radiation through a thickness of lead. They therefore recommended that 1 mgrm. of pure radium bromide should be regarded as a standard, and that the ionisation produced by the Gamma rays from that quantity after passing through 1 cm. of lead should be taken as the measure of the unit of radio-activity. They went on to suggest that multiples of this standard could then be prepared, feebly active standard solutions containing 1/10, 1/100, 1/1000 mgrm. of the active salt being conveniently obtained by the method described by Rutherford for comparisons based upon "emanation methods." The Committee was of opinion that a fundamental C.G.S. unit of radio-activity was not at present feasible, but suggested

that it might ultimately be possible to define the standard in C.G.S. units as that weight of radium which radiated energy at the rate of, say, one erg per second.

A number of interesting letters from well known scientists were read at the meeting, and revealed certain differences of opinion, principally on the question of the atomic weight of radium, the correct thickness of the lead screen to be used in filtering out the Alpha and Beta rays, and the purity of radium preparations. Professor Silvanus Thompson asked whether an organic reaction could be made use of as at least an approximate test of possible therapeutic effect—whether there was no coloured organic substance which would give a reaction in presence of radium. Sir William Ramsay wrote that, according to experiments now being carried out at University College, it appeared probable that the atomic weight of radium is more than 240. (Mdme. Curie's estimate was originally 225. and has been more recently modified to 226). It appeared to him that we must wait till we have a sample of radium bromide of undoubted purity which had been re-crystallised often. Prof. E. Rutherford suggested a lead screen thickness of 5 mm. instead of 1 cm., stating that the former thickness was sufficient to mask the inconstant rays, and would at the same time extend the lower limit of comparison of quantities of radium by this method. Prof. Rutherford added that he thought the Society would be doing a good work by fixing a temporary radio-active standard for radium, both for the advantage of physicists and professional men. The number of people in the past who had paid for pure radium and been given nearly pure barium was legion.

A discussion ensued, in which Mr. C. E. S. Phillips, replying to some of the criticisms in the letters, said that the choice of 1 cm. as the screen thickness was made because that distance was more easily expressed and remembered than an odd number of millimetres. Mr. F. H. Glew questioned whether the Committee had done wisely in selecting radium as the standard of radio-activity. He thought uranium would have been better. Mr. W. Duddell, the President, said that any standard of radio-activity must be constant and capable of reproduction. As in electrical work a practical sub-standard might be made and compared from time to time with the fundamental standard which it was hoped would be in the National Physical Laboratory.

NOTICES OF BOOKS.

Town Gas and its Uses. By William Hosgood Young Webber. London: Archibald Constable and Co., Ltd. 1907.

The well-informed general public will find that this book gives them an excellent opportunity of acquiring a knowledge of the manufacture and uses of town gas. The early history of the industry is narrated, and the difficulties with which it had to contend will provide food for thought on the part of that conservative section of the public which is always ready to oppose new schemes which appear to threaten old interests. A sufficiently detailed description of the interior of modern gas-works is given to enable the reader to form a clear idea of the general structure and arrangement of the plant, and the great importance of the by-products of the manufacture is emphasised. An excellent discussion of the different systems of lighting and the various burners upon the market is well illustrated by photographs, and in the chapter on the cost of gas lighting the construction and method of reading a meter are described. The author writes in glowing terms of the great advantages to be gained by the use of gas for heating and cooking, and possibly some of the figures given relating to both uses will surprise his readers. The healthfulness and safety of town gas and its use for power generation are considered in two chapters, in the latter of which an account is given of the value of an engine, supplied with town gas, for the generation of electricity for private installations. Finally, the author gives a short summary of the legal relations of gas suppliers, consumers, and the public, and clears up some common misapprehensions on this subject.

Die Flechtenstoffe. ("The Lichens.") By Dr. W. Zopf. Jena: Gustav Fischer. 1907.

This work is a pioneer in biochemical literature, being the first treatise yet published devoted exclusively to the lichen acids and their derivatives. The student who wishes to explore that inaccessible and little known region where botany and chemistry meet, has every reason to be grateful to Dr. Zopf for thus clearing the way for him. The book will probably be most appreciated by the botanist whose knowledge of chemistry is deficient. The first short section gives a summary of the chemical and physical properties of the lichen acids in general, and in the second section, which fills the greater part of the book, a detailed account is given of all the known substances belonging to this category. The occurrence of each acid and its preparation and properties are discussed, and the decomposition products, where these have been studied, are described in full. The following section on the physiology and biology of the lichens might well have been rather fuller and more detailed. The technical importance of those lichens which have application in dyeing is discussed in a short section, and an excellent index is provided. Although the author has had to adopt a somewhat restricted definition of lichen substances, and has only taken into account the crystallising lichen acids, his book is a valuable summary of the present state of our knowledge of a subject which possesses a very scattered literature, and which up to the present has found no competent chronicler.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 24, December 9, 1907.

Direct Hydrogenation of the Aromatic Diones.—Paul Sabatier and A. Mailhe.—Benzile, $C_6H_5.CO.CO.C_6H_5$, may be hydrogenated in presence of nickel by an excess of hydrogen at 220—230°. The reaction is complete, and the only products are water and symmetric diphenylethane or dibenzyl:—

$$C_6H_5.CO.CO.C_6H_5 + 4H_2 = C_6H_5.CH_2.CH_2.C_6H_5 + 2H_2O.$$

Under the same circumstances (temperature, 210—220°) benzoïn yields the same products. The β-dione, benzoylpropanone, when similarly reduced, yields chiefly butyl benzene,—

$$C_6H_5.CO.CH_2.CO.CH_3 + 4H_2 = C_6H_5.CH_2.CH_2.CH_2.CH_3 + 2H_2O,$$

as well as small quantities of hexahydrobutyl benzene.

Action of Incandescent Electric Conductor upon surrounding Gases.—M. Couriot and Jean Meunier.—Incandescent electric conductors of small diameter have been shown by the authors to be incapable of causing the explosion of mixtures of fire-damp and air, even under conditions most favourable to such explosions. The explanation now put forward for this phenomenon is as follows:—The incandescent filament attracts the molecules of oxygen and repels those of the hydrocarbon. Thus a sort of protective zone is formed round the filament, and as the molecules of hydrocarbon become fewer in the immediate neighbourhood of the filament, the concentration necessary for explosion is not reached. If, however, the

incandescent conductor is large enough it may radiate sufficient heat to penetrate this protective zone, and thus an explosion is caused.

Non-existence of a common Solvent for Yellow and Red Phosphorus.—Alb. Colson.—The author has investigated the action of essence of terebenthene upon the two varieties of phosphorus, and finds that, although it is a good solvent for yellow phosphorus, neither the liquid itself nor any polymer obtained from it by the action of heat, can dissolve the red variety. Since the vapours of the two modifications have the same density, corresponding to the molecule P_4, if it is assumed that the dissolved state is similar to the state of vapour, it would necessarily follow that if it were possible to dissolve it in essence of terebenthene it would be transformed into the yellow variety.

Apparatus for producing the Spark Spectra of Solutions.—A. de Gramont.—The negative electrode is surrounded by a capillary tube of fused silica, and a second capillary of the same material is arranged above the first, and inclined at an angle of 45° to it; this tube contains the positive electrode, and is fed with the liquid to be examined from a reservoir. The ends of the platinum electrodes are at least 5 mm. from the ends of the capillary tubes. The whole arrangement, to prevent splashing and loss of liquid, is surrounded by a glass tube fitted with a window for observing the spark. The vapours formed during the operation can be drawn off by gently heating a raised side tube connected with the glass tube.

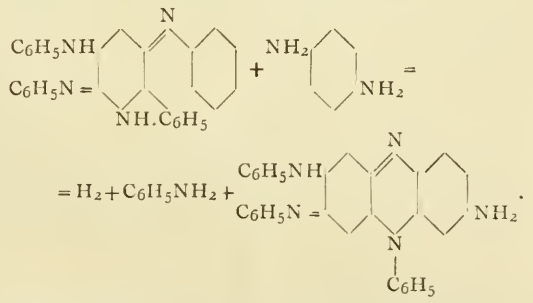
Graphite and Graphitic Carbon in Cast-irons.—Georges Charpy.—A specimen of cast-iron was liquefied and separated into two parts. One was allowed to solidify slowly, and thus grey cast-iron was obtained. The other part was cooled rapidly, thus forming white cast-iron, which was then tempered to form grey cast-iron. The carbon was separated in each case by dissolving out with boiling nitric acid, and it was then found that each specimen was transformed into graphitic acid at the same rate. Both specimens behaved similarly when subjected to the action of a current of hydrogen at 1000°. Thus graphite and graphitic carbon separated by tempering form a single phase in the iron-carbon systems.

Action of Gaseous PH_3 on Mercuric Chloride and Bromide.—P. Lemoult.—When gaseous PH_3 acts on mercuric chloride, care being taken to avoid the presence of excess of the gas even locally, a compound of the formula PHg_3Cr_3 is obtained. Mercuric bromide, however, gives a brown compound, the formula of which is $P_2Hg_5Br_4$. Apparently the reactions can be represented by the equations $PH_3+3HgCl_2=3HCl+PHg_3Cl_3$, $2PH_3+5HgBr_2=6HBr+P_2Hg_5Br_4$. To check these conclusions, since the analysis of the products presented considerable difficulties, the author determined how much mercuric salt was consumed by one molecule of PH_3, when the former was in excess. With the chlorine compound he found one molecule PH_3 used up 2·93 molecules $HgCl_2$, and with the bromine compound one molecule PH_3 = 2·54 molecules $HgBr_2$, which agrees very well with the theoretical numbers obtained from the equation. The chloride and bromide of mercury are excellent absorbers for the gas PH_3, and this fact might be employed in qualitative and quantitative analysis.

Transformation of Barbaloïn into Isomeric β-Barbaloïn.—E. Léger.—When barbaloïn is heated for three hours to a temperature of 160° to 165° it is converted into a modification β-barbaloïn. This modification does not crystallise, but readily yields a crystalline chlorinated derivative, the formula of which is $C_{21}H_{16}Cl_4O_9$. The chloride obtained from the original barbaloïn differs in crystalline form from this compound, and also contains one and a-half molecules of water. Thus aloïn is one of the numerous substances which are optically active and are transformed into their optical isomers under the action of heat. When the barbaloïn in Cape aloes is removed, and the amorphous residue is chlorinated, chlor-β-barbaloïn is obtained. Thus Cape aloes are much richer in aloïn than is generally supposed, but one part of the aloïn occurs in the amorphous or β-form. Other aloes, *e.g.*, those from Uganda, give the same result.

Dissociation of Compounds of Acid and Basic Dyes by Adsorbent Substances.—L. Pelet-Jolivet.—The aqueous solutions of basic dyes are precipitated by many acid dyes, the dye in excess determining the colour of the solution. A definite compound is thus obtained, which may be regarded as a compound of the basic dye with the organic residue of the acid dye. The molecular weight of these compounds, determined by the cryoscopic method in paratoluidine or phenol, is one-quarter to one-third lower than the theoretical molecular weight; hence, pronounced dissociation occurs. When adsorbent substances, such as wool or animal charcoal, are added to the aqueous solution of the coloursd compound, it is found that in neutral or faintly alkaline solution the adsorbent solid dissociates the coloured compound, and fixes only the basic element; the solution retains the colour of the acid dye. In acid solution the absorbent substance dissociates the compound, but fixes the acid dye, and the solution has the colour of the basic dye. The colloidal theory of dyeing explains these facts. The adsorbent substances are in the colloidal state. In a neutral or alkaline bath their charge is negative, and they precipitate and fix only the positive basic dye. In an acid bath the adsorbent is positively charged, owing to the H^+ ions of the acid added, and in this case fixes the negative acid dye.

Synthesis of Symmetrical Phenylated Anilido-phenosafranine.—Ph. Barbier and P. Sisley.—When an alcoholic solution of a mixture of azophenine and paraphenylene diamine is heated in a closed vessel to 165° for six or seven hours a violet-blue liquid is obtained, from which, by distillation in a current of steam, the symmetrical phenylated chlorhydrate of anilido-phenosafranine, $C_{30}H_{23}N_5.2HCl$, may be separated. The following scheme shows the formation of this substance.



Condensation of Water Vapour in presence of Radium Emanation.—Mdme. Curie.—The author has already shown that when a gas under atmospheric pressure contains radium emanation, the induced activity in suspension in the gas behaves like matter having weight, and the particles not only travel towards the wall but also have a slow movement downwards. This phenomenon may not occur when the gas is perfectly dry, and hence the author concluded that the presence of water vapour favours the formation of agglomerations which have as nuclei the particles of induced activity, and which may attain sufficient mass to acquire an appreciable downward velocity. Damp air containing radium emanation is always more or less opaque, owing to the presence of particles of mist which can easily be seen when it is lighted by an electric arc light. The air need not be saturated with moisture, but no mist is produced in perfectly dry air. When bulbs of 35 to 50 cc. capacity contained the maximum quantity of emanation furnished by a solution of 0·05 grm. of pure radium chloride, the conditions of the formation of the mist were as follows:—1. When the bulb contained a few cc. of distilled water. It was still visible after twenty

days. 2. When the bulb contained a solution of sulphuric acid in water. 3. When the bulb contained crystals of sodium phosphate, for which the equilibrium pressure of water vapour at 17° is about 1 cm. of mercury. 4. When the bulb contained a little phosphoric anhydride the mist appeared when the emanation was introduced, but disappeared in a day owing to the absorption of the water by the anhydride. 5. When the bulb contained a little petroleum ether and a small piece of phosphoric anhydride. The mist produced was much more marked than with distilled water. The bulbs contained two platinum electrodes. If a difference of potential of some hundreds of volts was established between these electrodes the mist disappeared. This action of the electric field seems to show that the condensation of vapour occurs round the particles of induced radio-activity which in an electric field move rapidly towards the cathode. On the suppression of the field the mist re-forms, becoming visible in five minutes. If the bulb contained distilled water and air, but no emanation, the little drops of moisture formed round any dust present on the least variation in temperature. These drops, however, were rapidly deposited, and new droplets were formed only with difficulty and in very small numbers. From these experiments it must be concluded that the particles of induced radio-activity of radium possess the property of condensing water vapour, either by electrostatic attraction or by chemical affinity. The same phenomenon is observed with the vapour of petroleum ether; it must not be confused with the phenomenon of the condensation of vapour by the gaseous ions which are produced in large numbers by radium emanation. In this case the condensation only occurs when the pressure of the water vapour becomes momentarily about four times as great as the equilibrium pressure.

MISCELLANEOUS.

The late Lord Kelvin.—In an appreciative obituary notice of Lord Kelvin, which appeared in a recent number of the *Chemiker Zeitung*, an unfortunate error has been perpetrated. Owing, no doubt, to the similarity of surname, confusion has arisen between the late Lord Kelvin and Prof. J. J. Thomson, who is still happily with us, and in the full tide of activity of mind and body. The error is perhaps the more painful and serious in that it occurs, not in the letterpress, in which a laudatory account of Lord Kelvin's achievements is given, but in the accompanying portrait, which is that of the distinguished Professor of Experimental Physics at the University of Cambridge.

NOTES AND QUERIES.

Electrolytic Deposition of Bismuth.—I should be greatly obliged if any of your readers could give me the following information:—(*a*) The best solution for electrically depositing bismuth from. (*b*) Best current density for depositing. (*c*) Is the oxide of bismuth conductive to the electric current, like that of silver?—E. G. Middleton.

MEETINGS FOR THE WEEK.

Monday, 20th.—Society of Arts, 8. (Cantor Lecture). "Theory and Practice of Clock Making," by H. H. Cunynghame, C.B.

Tuesday, 21st.—Royal Institution, 3. "The Internal Ear of different Animals," by Dr. A. E. Gray, F.R.S.E.

—— Society of Arts, 8. "The Art of Jewellery," by Mrs. Hadaway.

Wednesday, 22nd.—Society of Arts, 8. "Siam and its People," by Harry Hillman.

Thursday, 23rd.—Royal Institution, 3. "Recent Light on Ancient Physiographies," by Prof. W. W. Watts, F.R.S.

Friday, 24th.—Royal Institution, 9. "The Extinction of Malta Fever," by Col. David Bruce.

—— Physical, 5. "Recalescence Curves," by W. Rosenhain. "An Experimental Examination of Gibbs' Theory of Surface Concentration regarded as the Basis of Adsorption, and an application to the Theory of Dyeing," by W. C. M. Lewis.

Saturday, 25th.—Royal Institution, 3. "The Electrification of Railways," by Prof. Gisbert Kapp, Dr.Eng., M.Inst. C.E.

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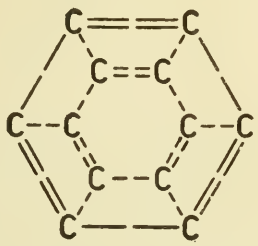
THE CHEMICAL NEWS.

Vol. XCVII., No. 2513.

NOTE ON THE CONSTITUTION OF THE CARBON MOLECULE FROM THE STANDPOINT OF THERMO-CHEMISTRY.

By H. STANLEY REDGROVE, B.Sc., F.C.S.

Prof. Sir James Dewar has recently brought forward the interesting suggestion (Chemical News, xcvii., 19) that the constitution of the carbon molecule is represented by the formula—



It will be of interest to see how far this formula is supported by thermo-chemical data.

Using the author's notation (Chemical News, xcv., 193 and 301), the heat of combustion of a grm.-mol. of carbon is represented by $12\alpha - 12\beta - 6\gamma = 2529{\cdot}6$ cals. $- 630{\cdot}0$ cals. $- 534{\cdot}0$ cals. $= 1365{\cdot}6$ cals. Accepting the value 97·0 cals. as the atomic heat of combustion of carbon we we get 1164·0 cals. for the molecular heat of combustion, assuming that the carbon molecule contains twelve atoms, as above. The above formula therefore gives an error of 201·6 cals.

The formula is derived from the fact that, on oxidation of carbon, mellitic acid can be obtained, but it also assumes that Kekulé's formula is the true one for benzene derivatives, or at least mellitic acid.

Without making this assumption as to the nature of the benzene molecule, suppose the carbon molecule to consist of two condensed benzene molecules, its molecular heat of combustion would be represented by twice the molecular heat of combustion of benzene -63 cals. $= 2 \times 797{\cdot}9$ cals. (*i.e.*, Thomsen's experimental value corrected for constant volume) $- 315{\cdot}0$ cals. $= 1280{\cdot}8$ cals.

The error in this case is therefore 1280·8 cals. $- 1164{\cdot}0$ cals. $= 116{\cdot}8$ cals. This is a large error, but much less than when Kekulé's formula was assumed. In both cases the effect of the intramolecular tension due to the tetramethylene rings has been neglected; the effect would be to increase the molecular heat of combustion, and thus the errors are actually greater than the above.

The general formula for a carbon molecule containing "single" links only is $n(\alpha - 2\beta)$, with a molecular heat of combustion of 105·8 n cals. The most likely of these formulæ from the mellitic acid standpoint is $12\alpha - 24\beta$, with a molecular heat of combustion of 1269·6 cals., giving an error of 105·6 cals., which is also large. Such a carbon molecule could be derived from either Ladenburg's or Claus's benzene formulæ, but in each of these intramolecular tension would be introduced, which would cause the error to be higher; such a formula as $12\alpha - 24\beta$, or, indeed, any formula for the carbon molecule, without intramolecular tension appears to be geometrically impossible. It is, of course, not unlikely that the various modifications of carbon may possess different molecular structures. A perfectly satisfactory solution of the benzene mystery and a fuller knowledge of valency might, however, throw light on the question of the constitution of the carbon molecule.

The Polytechnic, Regent Street, W.

A PHYSICO-CHEMICAL STUDY OF THE COMPLEX COPPER-GLYCOCOLL SULPHATES.*

By J. T. BARKER, B.Sc.

It is well known that addition of glycocoll to aqueous solutions of copper sulphate produces a fine blue colour, similar in general character to that produced by excess of ammonia. That the concentration of the cupri-ions has been lowered by the presence of the glycocoll is rendered probable by the fact that caustic potash does not precipitate cupric hydroxide from solutions containing moderate amounts of glycocoll, whereas potassium ferrocyanide and ammonium hydrosulphide throw down precipitates of cupric ferrocyanide and sulphide respectively. It seemed probable that the reduction in the concentration of the cupri-ions is caused by the formation of complex cupri-glycocoll cations. The experimental work described in the present paper was undertaken with the object of investigating this question.

1. *Electrometric Measurements.*

In order to arrive at some idea of the degree of complex formation, the following preliminary measurements of potential were made:—A series of solutions one-tenth molecular normal with respect to copper sulphate, but respectively $n/2$, $n/5$, $n/10$ with respect to glycocoll, was made up. By Poggendorff's compensation method, using a slide-wire bridge and a Lippmann capillary electrometer, the potential difference between a clean copper rod and each of these solutions was determined. For this purpose each copper electrode was connected through a KCl solution with a normal calomel electrode, and the cells so constructed were measured with and against a standard cadmium cell in the usual manner. Taking the potential of the calomel electrode as $+0{\cdot}56$ volt, and the E.M.F. of the cadmium cell as 1·0186 volt, the results shown below were obtained at 17° C.

In calculating these values the potentials at the liquid junctions have been neglected (as a first rough approximation).

By means of the formula $\pi = \frac{0{\cdot}000198\,T}{2} \log \frac{c_1}{c_2}$ we can now obtain approximate values for the ratios of the cupri-ion concentrations in the several solutions examined. In the above formula π denote the E.M.F. of a cell such as—

$$Cu \mid CuSO_4 \mid KCl \mid CuSO_4 + \text{glycocoll} \mid Cu,$$

and c_1 and c_2 denote the respective cupri-ion concentrations.

Solution.		Potential of copper electrode (volt).
Concentration of $CuSO_4$.	Concentration of glycocoll.	
$n/10$	0	$+0{\cdot}558$
$n/10$	$n/10$	$+0{\cdot}549$
$n/10$	$n/5$	$+0{\cdot}537$
$n/10$	$n/2$	$+0{\cdot}512$

Thus for the cell Cu | $n/10 - CuSO_4$ | KCl | $n/10\,CuSO_4 + n/10$ glycocoll | Cu $\pi = 0{\cdot}558 - 0{\cdot}549 = 0{\cdot}009$ volt.

Calling the concentration of the cupri-ion in the $n/10 - CuSO_4$ solution 100, we obtain in this way the relative values given in Table I.

These figures, though not pretending to be very accurate, suffice to show the progressive decrease of the $Cu^{\cdot\cdot}$-concentration on continued addition of glycocoll, and appear to

* A Paper read before the Faraday Society, December 17, 1907. From the Muspratt Laboratory of Physical and Electro-chemistry, University of Liverpool. Communicated by Dr. F. G. Donnan.

warrant the assumption that with a large excess of glycocoll the cupri-ion will be practically completely converted into some complex ion (or neutral compound).

TABLE I.

Molar ratio of glycocoll to $CuSO_4$.	Relative concentration of $Cu^{\cdot\cdot}$-ion.
0	100
1	48
2	19
5	3

We shall assume first of all, as seems most probable, that a complex cupri-glycocoll ion cation is formed, and that its formula may be represented as $CuG_x^{\cdot\cdot}$, *i.e.*, that it contains x mols. of glycocoll for every atom of copper. If the glycocoll be present in large excess relatively to the copper sulphate, we may assume, with a fair degree of probability, that practically all the copper sulphate will be converted into complex copper-glycocoll sulphate, and that, to a first approximation, we may take the final concentration of the glycocoll as equal to its initial concentration. Furthermore, if the solution be pretty dilute with respect to total dissolved copper salts, the complex sulphate (or sulphates) may be regarded as completely ionised, in which case the final molar concentration of the cupri-glycocoll ion will be equal to the initial molar concentration of the copper sulphate. Let us suppose that the complex ion $CuG_x^{\cdot\cdot}$ dissociates (non-electrolytically) into glycocoll and cupri-ions. Denoting molar concentrations by square brackets, and writing i for initial total concentration of copper sulphate, we have—

$$[Cu^{\cdot\cdot}]_1.[G]x = k[CuG^{\cdot\cdot}{}_x]_1 = ki_1.$$

For another solution—

$$[Cu^{\cdot\cdot}]_2.[G]_2 = ki_2.$$

Whence, dividing and taking logarithms—

$$\log \frac{[Cu^{\cdot\cdot}]_1}{[Cu^{\cdot\cdot}]_2} + x \log \frac{[G]_1}{[G]_2} = \log \frac{i_1}{i_2} \quad . \quad . \quad 1.$$

Although $[Cu^{\cdot\cdot}]_1$ and $[Cu^{\cdot\cdot}]_2$, may be very small, their ratio is a definite quantity, which is found by measuring the potentials of a copper electrode in each of the two solutions, and then applying the formula—

$$\pi = \frac{RT}{2F} \log \frac{[Cu^{\cdot\cdot}]_1}{[Cu^{\cdot\cdot}]_2}.$$

The only unknown quantity in Equation 1 is, then, x. In order to obtain the most accurate values, two corrections must be applied to Equation 1. In the first place, an allowance must be made for the amount of free glycocoll removed from the solution as complex ion; and, secondly, if the complex copper-glycocoll sulphate be not completely ionised, the concentration of the complex copper-glycocoll ion is not equal to the initial total concentration of copper sulphate. The second correction will be dealt with later.

Equation 1, with the first correction, takes the form—

$$\log \frac{[Cu^{\cdot\cdot}]_1}{[Cu^{\cdot\cdot}]_2} + x \log \frac{[G]_1 - xi_1}{[G]_2 - xi_2} = \log \frac{i_1}{i_2} \quad . \quad . \quad 2.$$

In solving this equation, an approximate value of x is first obtained from Equation 1, and then the value of x which satisfies 2 is found by successive approximations.

In the case of the preliminary data already given, any potential differences existing at the liquid junctions were ignored. These potential differences can probably be for the most part eliminated by comparing only solutions having the same total copper content and a varying, though very large, relative excess of glycocoll; for in this case the two solutions will contain practically only complex sulphate, and that of practically the same concentration in both cases. It will be seen that the method here employed is substantially that first introduced by Bodländer.

The results of the first measurements are contained in the following two tables. The E.M.F's. of the concentration cells have been calculated from direct measurements of cells of the type Cu | $CuSO_4$ + glycocoll | $3{\cdot}5\,n - NaNO_3$ | calomel electrode.

The value 1·35 is evidently too low. For the rest, the values of x given in Table III. are seen to be considerably higher than those in Table II. Probably only the values in Table III. are deserving of weight, since these are derived from measurements of pairs of solutions of equal total copper content.

TABLE II.—*Temperature* 13° C.

First solution.		Second solution.		E.M.F. of combination.	x Calculated from Equation 1.
$CuSO_4$.	Glycocoll.	$CuSO_4$.	Glycocoll.		
$n/200$ +	$n/1$	$n/100$ +	$2n$	0·0138	2·62
$n/200$ +	$n/2$	$n/100$ +	$n/1$	0·0030	1·35
$n/200$ +	$n/2$	$n/100$ +	$2n$	0·0421	2·97
$n/200$ +	$n/1$	$n/100$ +	$2n$	0·0135	2·58

TABLE III.—*Temperature* 13° C.

$n/100$ +	$n/1$	$n/100$ +	$2n$	0·0351	4·12
$n/100$ +	$n/1$	$n/100$ +	$2n$	0·0391	4·59
$n/200$ +	$n/2$	$n/200$ +	$n/1$	0·0289	3·39

More accurate measurements were now carried out, in which every effort was made to eliminate disturbing influences. The calomel electrode was dispensed with, the E.M.F's. of the concentration cells being directly measured with $3{\cdot}5n$ $NaNO_3$ solution as connecting liquid. The concentration cell was combined with a standard cadmium cell, and the E.M.F. of this combination determined, with the concentration cell acting both with and against the cadmium element. From these measurements the E.M.F. of the concentration cell was calculated. The means of the two values so obtained are given in the following table. As the E.M.F's. of the concentration cells do not amount to more than 3 to 4 hundredths of a volt, and small errors in the values of the E.M.F's. produce considerable errors in the values of x, it was found necessary to introduce corrections for any inequality of potential of the two copper electrodes when dipping in the same copper solutions. This inequality of potential did not ever appreciably exceed 1 millivolt. On making this correction, it was found that the values whose means are given in the following table did not differ by more than a few tenths of a millivolt. In order to eliminate errors due to the liquid potentials or to a varying degree of ionisation of the complex sulphate, only solutions of the same total copper content were compared, and these solutions contained large relative excesses of glycocoll.

Since $i_1 = i_2 = i$, Equations 1 and 2 reduce to—

$$\log \frac{[Cu^{\cdot\cdot}]_1}{[Cu^{\cdot\cdot}]_2} + x \log \frac{[G]_1}{[G]_2} = 0 \quad . \quad . \quad 3.$$

$$\log \frac{[Cu^{\cdot\cdot}]_1}{[Cu^{\cdot\cdot}]_2} + x \log \frac{[G]_1 - xi}{[G]_2 - xi} = 0 \quad . \quad . \quad 4.$$

TABLE IV.—*Final E.M.F. Measurements.*

Concentration of $CuSO_4$ in both solutions.	$[G]_1$.	$[G]_2$.	E.M.F. of concentration cell.	Temperature.	x Calculated from 3.	x Calculated from 4.
$n/80$	$5n/2$	$5n/4$	0·0335	19°	3·85	3·75
$n/100$	$2n$	$n/1$	0·0339	19°	4·12	4·00
$n/200$	$n/1$	$n/2$	0·0355	20·5°	4·05	3·95
$n/250$	$4n/5$	$2n/5$	0·0318	20·5°	3·63	3·54
$n/250$	$4n/5$	$2n/5$	0·0309	21°	3·53	3·45
$n/300$	$2n/3$	$n/3$	0·0327	19°	3·76	3·65
			Mean values		3·82	3·72

It will be observed that the ratios of glycocoll to copper sulphate are the same for the different pairs of solutions, so that any pair of solutions could be obtained from a more concentrated pair by dilution. This was done with the intention of seeing whether the value of x varied with the

dilution, the ratio of glycocoll to copper sulphate being constant. No variation within the above range of concentrations can be said with certainty to occur.

The E.M.F. measurements point to the existence of complex ions of the formula $[CuG_4]^{\cdot\cdot}$ and their dissociation products. To this ion corresponds the complex sulphate $[CuG_4]SO_4$. The fact that x comes out somewhat less than 4 is probably due to the partial dissociation of the complex ion $CuG_4^{\cdot\cdot}$ into less complex ions such as CuG_3, &c., *i.e.*, the elementary $Cu^{\cdot\cdot}$-ions are converted by the excess of glycocoll partly into complex ions containing less glycocoll than $CuG_4^{\cdot\cdot}$.

This conclusion requires to be supported by evidence obtained from some independent method, and with this object in view the freezing-point measurements described in the next section were undertaken.

2. *Freezing-point Measurements.*

A few preliminary measurements of the freezing-points of aqueous glycocoll solutions gave as a mean value for the molecular weight 73·5 (theoretical value, 75), thus confirming the already known result that glycocoll exists *substantially* as simple molecules in aqueous solution.

In order to investigate the complex formation, the freezing-points of a series of strong glycocoll solutions of gradually decreasing concentration were determined, and the *rise* of freezing-point produced by the addition of small quantities of copper sulphate to these solutions measured very carefully. Let γ denote the net number of active individuals removed from the solution per mol. copper sulphate added. As before, let x denote the number of glycocoll molecules which combine with the Cu-atom to form a complex. We shall now assume that practically all the copper sulphate added is converted by the large excess of glycocoll present into complex sulphate, and that at the fairly high dilution used the value of van't Hoff's factor i for the complex sulphate is the same as that for copper sulphate of the same total molar concentration. Then, per grm. mol. copper sulphate added, i new individuals enter the solution, whilst x individuals (glycocoll molecules) are removed. Hence $x-i=\gamma$, or $x=\gamma+i$. If the solution employed is so dilute with respect to total copper that we can assume complete ionisation of the complex or simple sulphate, $x=\gamma+2$.

The practical range of this method of procedure is limited by the following considerations:—The rise of freezing-point actually measured being dependent upon the amount of $CuSO_4$ present, as much of this salt as possible must be added, in order to reduce the percentage error of the readings. But as it is imperative to have the glycocoll in large excess of the copper sulphate to ensure as complete as possible a formation of complex salt, the amount of copper salt that can be added will depend on the solubility of glycocoll at the temperature of the freezing-points. The cryohydrate point of glycocoll was found to be approximately $-3°$, so that at this temperature the saturated glycocoll solution must contain about 2·3 grms. of glycocoll per 20 grms. water. In the experiments to be described the amount of glycocoll taken varied from 1·2 to 2·1 grms. per 20 grms. water, whilst the rises of freezing-point observed varied from 0·021° to 0·088°. Supposing the probable error of any one reading to be 0·001° and of any measured rise to be 0·002°, the percentage error of the latter must vary from 9·5 per cent to 2·3 per cent.

In order to obtain values of x of sufficient accuracy for our purpose it is clearly necessary that the rises of freezing-point must be determined very carefully. In the apparatus used the cooling bath of ice and brine was surrounded by a vessel containing finely crushed ice, the outer walls of which were enveloped in felt, so that its temperature did not vary as much as one-tenth degree during a series of measurements. The stirring was done by an automatic stirrer driven at a constant rate, the Beckmann thermometers were kept in ice for several hours before a measurement, and for every series of measurements with one solution the temperature of the ice-brine bath was carefully adjusted so as to give a convergence-temperature as nearly as possible equal to the freezing-point to be measured. The supercooling was kept within the limits 0·1—0·2°. The following example well shows the general accuracy of the results:—

Freezing-point of Pure Glycocoll Solution.

Temp. of cooling bath.	Freezing-point.	Supercooling.
−4·5°	2·393	0·178°
−4·5°	2·390	0·150°
−4·5°	2·392	0·167°
−4·5°	2·394	0·162°
Mean ..	2·392	

Freezing-points of Glycocoll-copper Sulphate Solution.

−4·5°	2·415	0·175°
−4·5°	2·413	0·171°
−4·5°	2·412	0·157°
Mean ..	2·413	

Rise of freezing-point = 0·021°.
Concentration of copper sulphate = 0·000886 grm. mol. per 100 grms. water.
i for copper sulphate at this dilution = 1·89.
Total number of mols. glycocoll present in the solution per mol. $CuSO_4$ = 89·5.
Calculated value of x = 3·17.

The following table contains the results of the freezing-point measurements.

TABLE V.—*Freezing-point Measurements.*

Concentration of $CuSO_4$ in grm. mols. per 100 grms. water.	Mols. glycocoll per mol. of $CuSO_4$.	Rise of freezing-point.	Values of i for $CuSO_4$.	Values of x when— i for complex salt has same value as for $CuSO_4$.	Values of x when— i for complex salt is taken as 2.
0·000886	89·5	0·021°	1·89	3·2	3·3
0·00146	84·4	0·0355°	1·81	3·1	3·3
0·00194	63·5	0·0555°	1·75	3·3	3·5
0·0023	60·6	0·055°	1·70	3·0	3·3
0·00182	54·4	0·0393°	1·76	2·9	3·2
0·00297	46·5	0·072°	1·63	2·9	3·3
0·00346	40·0	0·0885°	1·59	3·0	3·4
0·00298	33·3	0·0643°	1·64	2·8	3·2
		Means		3·0	3·3

The values of i for solutions of $CuSO_4$ have been previously determined, but it was deemed advisable to redetermine these cryoscopically for the present purpose, so as to ensure a high degree of comparability in the measurements. The values given in the above table have been obtained by graphical interpolation and extrapolation from the following measurements:—

TABLE VI.

Concentration of $CuSO_4$ in mols. per 100 grms of water.	Lowering of freezing-point.	Value of i.
0·0031	0·095°	1·62
0·0067	0·172°	1·38
0·0109	0·247°	1·22
0·0194	0·407°	1·14
0·0227	0·457°	1·09
0·0264	0·523°	1·07

The values of x in Columns 5 and 6 of Table V. do not differ to any very considerable extent. The true mean will lie undoubtedly between 3·0 and 3·3. It will be observed that this number is considerably lower than 3·72, the mean of the values obtained from the electrometric measurements recorded above. This divergence admits, however, of explanation, when we consider that for the solutions used for the cryoscopic measurements the ratio of mols.

glycocoll to mols. $CuSO_4$ varied from 33 to 89, whilst in the case of the solutions employed in the electromotive force measurements, this ratio varied from 100 to 200. It is to be expected that in the former case the non-electrolytic dissociation of the complex ion or ions would be greater owing to the smaller excess of glycocoll present. In accordance with this explanation, it will be seen that the values of *i* given in Column 5 of Table V. show a general tendency to decrease with decreasing values of the ratio mentioned above.

3. *Further Electrometric Measurements.*

In order to obtain a more direct comparison between the results of the electrometric and cryoscopic measurements, pairs of solutions were taken in which the molar ratios of glycocoll to copper sulphate were 30 and 90. In other respects the same procedure was followed as described under the final measurements of Section 1 of this paper. The results obtained are given in the following table :—

TABLE VII.—*E.M.F. Measurements in Solutions diluter with respect to Glycocoll.*

Concentration of $CuSO_4$ in both solutions.	Concentration of glycocoll in— First solution.	Second solution.	E.M.F. of combination.	Temp.	Value of *x* from— Equation 3.	Equation 4.
n/80	3*n*/8	9*n*/8	0·0458	14°	3·38	3·15
n/80	3*n*/8	9*n*/8	0·0471	11°	3·51	3·30
n/160	3*n*/16	9*n*/16	0·0390	12°	2·90	2·75
n/160	3*n*/16	9*n*/16	0·0422	14°	3·12	2·95
				Mean totals	3·23	3·04

The mean value of *x* calculated from these E.M.F. measurements agrees very well with the mean value obtained from the freezing-point measurements, which shows that the explanation of the previously noted divergence given at the end of Section 2 is probably the correct one.

(To be continued).

A NEW COLOUR TEST FOR MOLYBDENUM.

By WILLIAM BETTEL.

In 1903, while engaged upon the examination of so-called "refractory" ores containing molybdenum, I had occasion to add hydrogen peroxide to an aqueous solution of ammonium molybdate, rendered faintly alkaline with ammonia, with a view to converting the lower oxides of molybdenum —colouring the solution blue—into molybdate. The result of the experiment was the production of an intense brownish red colour (slightly redder than the colour produced by the Nessler test in weak ammonia solutions), the salt produced being, presumably, a permolybdate. This reaction, I believe, has not hitherto been published. On testing a sample of "chemically pure" ammonium molybdate with peroxide of hydrogen, one merely obtains the yellow colour (permolybdic acid ?) given by acid solutions of molybdenum trioxide when treated with hydroxyl. On rendering the solution slightly alkaline with ammonia, the yellow colour is replaced by the reddish brown colour previously observed. This colour is partly discharged by dilution, and disappears on standing, oxygen being evolved.

The colour is instantly discharged by addition of excess of alkalis; a moderate excess of ammonia has little action on the colour, but a large excess of ammonia discharges it. The colour is produced in aqueous solutions of alkaline molybdates (K and Na), quite neutral, or containing a mere trace of free alkali; this reaction is therefore a good indicator of neutrality when forming neutral molybdates.

For detection of molybdenum the solution to be tested is evaporated nearly to dryness, tested for neutrality by litmus; if alkaline, neutralised by nitric or sulphuric acid and solution of peroxide of hydrogen added. If a yellow colour is observed, add a small drop of dilute ammonia; the brownish red colour will then appear if molybdates are present.

To test the delicacy of the reaction various amounts of a standard solution of ammonia molybdate containing 5 mgrms. MoO_3 per 100 cc. were taken, evaporated to nearly dryness in porcelain capsules, cooled, the small drop rendered faintly ammoniacal, and two drops of a 5 per cent solution of pure peroxide of hydrogen added.

1. = 0·00005	grm. MoO_3	Strong reaction.
2. = 0·000005	,,	Distinct reaction.
3. = 0·000001	,,	Very faint tint, unmistakeable reaction.

Although I have found this reaction useful for approximately estimating molybdenum in rocks and ores, the instability of the permolybdates renders the method unsuitable for *accurate* quantitative work.

As a confirmatory test in qualitative analysis, and for detecting the presence and approximately estimating the percentage of molybdenum in tungsten trioxide, obtained in analysis of scheelite, wolframite, hubnerite, and other tungsten minerals, the reaction has frequently been made use of in my laboratories since 1903, with satisfactory results.

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THE CORROSION OF IRON AND STEEL.

By WILLIAM H. WALKER, ANNA M. CEDERHOLM, and LEAVITT N. BENT.

(Concluded from p. 33).

Ferroxyl Indicator.—That the corrosion of iron is an electrolytic phenomenon is shown by a very simple experiment devised by Dr. Allerton S. Cushman and ourselves. A piece of iron is immersed in ordinary water to which has been added a little phenolphthalein and a trace of potassium ferricyanide. Within a very few minutes the iron is seen to divide itself into zones or surfaces which exhibit opposite polarity. Those portions where the iron is anodic will become coated with a precipitate of Turnbull's blue, owing to the escape of the iron ions at those points. Those portions on which hydrogen is being liberated, acting as cathodes, will become bright red owing to the formation of hydroxyl ions. This action may be more easily studied if this reagent (for which Dr. Cushman has proposed the name "ferroxyl") be thickened by the addition of neutral gelatin or agar-agar. We will return to this phenomenon later in this paper.

Function of Oxygen.—The rapidity with which iron will pass into solution in water depends not only upon the electrolytic solution pressure of the iron and hydrogen, and the osmotic pressure of the iron ions already in solution, but also upon the "excess voltage" (uberspannung) which is required in order that the hydrogen ion which passes from the ionised condition may be set free (Nernst, *Theoretische Chemie*, 5th Ed., p. 712). In this case there is a counter electromotive force which must be overcome before the hydrogen can be liberated. It is possible, therefore, that the quantity of iron which can dissolve in water is limited to that amount which is equivalent to the hydrogen necessary to polarise that portion of the specimen which acts as the cathode. If this is the case, we should be able to make this solvent action continuous by the addition of any reagent which will depolarise the hydrogen-covered cathode portion. This reaction may be shown by the following very simple apparatus.

* Read before the New York Section of the American Chemical Society, May, 1907. From the *Journal of the American Chemical Society*, xxix., No. 9.

Two unglazed porcelain cups are placed concentric with each other and within a small Mason fruit jar, in the zinc top of which is soldered a small piece of copper tubing. The three vessels are filled with hundredth-normal potassium chloride solution free from oxygen and carbon dioxide, and the whole placed upon a hot plate of a temperature to insure continuous boiling. Two pieces of clean, pure iron, joined by an iron wire, are introduced into the central and outside compartment, and the whole while still boiling is sealed by screwing on the metallic cap. Hydrogen is allowed to enter the jar as it cools, in order to relieve the vacuum and prevent leakage of air. Such a cell may be maintained many hours without dissolving enough iron in either compartment to be detected by potassium ferricyanide in its unconcentrated condition. When reduced to a few drops, however, iron may always be shown to be present. Portions of each iron plate may be assumed to be anodic with iron tending to go into the ionised form, and other portions cathodic, being polarised by a film of hydrogen. If, now, a substance which will dissolve away the hydrogen be added to one compartment, the cathodic portion of the iron contained therein should be depolarised and the action should result in the solution of the anodic portions. Since the two pieces of iron are short-circuited above by a wire, and below by the electrolyte, that piece which is continually depolarised would be expected to become the cathode, and the other the anode. Hydroxylamine serves as such a depolariser, and from an apparatus as above described, after standing for forty-five hours at room temperature, the following results were obtained :—

	Blank.	Hydroxylamine.
Increase in weight of cathode	0·0005 grm.	0·0380 grm.
Decrease in weight of anode	0·0002 ,,	0·0393 ,,

When a 5 per cent solution of potassium dichromate is used as a depolariser, and the cell allowed to stand at room temperature for forty hours, the results were :—

	Blank.	$K_2Cr_2O_7$.
Increase in weight of cathode	0·0001 grm.	0·0212 grm.
Decrease in weight of anode	0·0000 ,,	0·0217 ,,

By passing a stream of hydrogen gas through all three cups iron will not dissolve in six hours sufficiently to give directly the ferricyanide test. If the hydrogen stream in one compartment be replaced by oxygen, iron will immediately begin to dissolve at an appreciable rate in the other compartment, separated though it is by the intermediate compartment through which hydrogen is passing. The dissolved iron in the anode compartment remains in solution as a ferrous salt, while the cathode compartment becomes strongly alkaline. If the porous cells be withdrawn, the iron at once oxidises and is precipitated as brown ferric hydroxide.

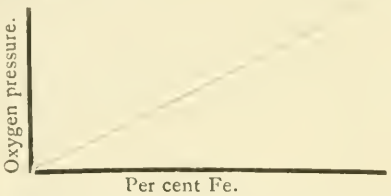
Mr. J. A. Collins, in a thesis presented at the Institute in 1898, noted the fact that if a piece of iron and a piece of magnetic oxide be immersed in water and connected through a voltameter, a very appreciable current would flow through the system with the iron as anode. To determine whether oxygen was a factor in this process the following experiment was performed. In a Jena flask containing hundredth-normal potassium chloride were suspended by fine platinum wires a piece of pure iron and a piece of magnetic oxide. These suspending wires were connected through a silver voltameter. By fitting the flask with a stopper containing gas inlet and outlet tubes, the operation could be carried on in either a vacuum or in any desired atmosphere. When all air and carbon dioxide were expelled by long boiling, and the flask cooled under conditions which preserved the vacuum, no current passed through the voltameter upon closing the switch. When connected through a Lippmann electrometer, however, a difference of potential between the two pieces was apparent. The electromotive force of the system is obviously not sufficient to furnish the "excess voltage" necessary to iberate the hydrogen on the magnetic scale, and while there exists this marked difference of potential, no appreciable current passes. If the concentration of the hydrogen ions be increased, as can be accomplished by saturating the water with carbon dioxide, the electromotive force is then sufficient to overcome this resistance and a measurable current is obtained, the iron passing into solution. If, on the other hand, air free from carbon dioxide be passed into the flask, the cathodic film is depolarised by the oxygen and the iron dissolves. As a secondary reaction, the oxygen oxidises, and the hydroxyl set free at the cathode precipitates the dissolved iron with the deposition of rust; this formation of rust is a factor in corrosion, however, only in so far that the concentration of the iron ions is kept very low, and hence its osmotic pressure is negligible.

The influence of the depolarisation action of oxygen may be conveniently studied by using the ferroxyl indicator. For example, in a beaker may be placed a porous earthenware cell, and the whole filled with ordinary water containing phenolphthalein and a very little ferricyanide. If a piece of iron be placed within the cell and connected by means of an iron wire with a piece of platinum in the outside compartment, immediate action takes place, deep red appearing on the platinum and a coating of blue precipitating on the iron. If, however, the platinum be heated in an alkaline pyrogallate solution, washed in boiling distilled water, and while wet used as the cathode in the cell, no action will take place for a number of hours. Only as the platinum takes up oxygen from the atmosphere does the reaction becomes apparent.

The influence upon the rate of solution of iron which different metals exercise when connected by a metallic conductor with the iron, is also easily shown by this method. Those metals in the electrochemical series more negative than iron influence the action, not in proportion to their relative position in the series, but rather in proportion to some other property, possibly their ability to occlude or condense oxygen. On the other hand, aluminium is much less active in protecting iron than is zinc although it is more electro-positive, while manganese completely reverses the polarity, making the iron the cathode and itself dissolving rapidly with the formation of brown manganese hydroxide.

Another conception of this action which differs only in the point of view from the above, is to consider the metal which acts as a cathode, for example, the platinum, as an oxygen electrode, and that the current flowing through the circuit (on account of which the iron dissolves) is due to the solution of oxygen and the formation of hydroxyl ions charging the solution negatively, and thereby requiring a solution of iron at the other electrode to bring about electrostatic equilibrium. When viewed in either of these two lights, the action should be proportional to the concentration of oxygen in the solution, and hence, according to the laws of Henry and Dalton, to the partial pressure of the oxygen in the atmosphere above the solution. An experiment to test this conclusion was performed as follows :—A number of Jena flasks were partly filled with boiled water and connected by means of a by-pass to a reservoir filled with definite mixtures of oxygen and nitrogen, freed as far as possible from carbon dioxide by being washed through strong potassium hydroxide and stored over barium hydroxide solution. When the water in the flasks was boiling violently, equal weights of pure iron were introduced, and after ten minutes further boiling, the exit tubes were sealed, and by means of the by-passes, each flask as it cooled drew from the reservoir with which it was connected an atmosphere of known composition. Two or three times each day the gas over the solution was changed by passing through the flask a quantity of gas from the reservoir. At the end of a few hours the difference in the rapidity with which the iron was attacked was easily apparent, and after standing for four or five days the wire in each flask was cleaned and weighed. Any oxide which adhered to the wire was reduced in hydrogen and the wire again weighed. The loss of iron was in this way calculated, and the results shown in the

plot. The rate of the reaction is thus seen to be a direct function of the oxygen pressure, and it is to be noted that the curve passes through the zero point. Only that



amount of carbon dioxide which will not be absorbed by strong caustic alkalis could have been present, and this amount must have been constant in each flask. If the presence of carbon dioxide is an important factor in corrosion, it is difficult to understand why the solvent action should be so independent of the amount of carbon dioxide present. Although the same weight of iron was added to each flask, there was not the same area undergoing active corrosion in each case. There were always clearly defined cathodic portions on each wire, which remained perfectly bright, and on which the hydrogen was being deposited and the oxygen absorbed. These differed markedly in the different specimens, but did not seem to bear a definite relation to the pressure of oxygen. When phenolphthalein was present, the bright spots were seen to continue to maintain a red zone in the solution around them. This irregularity in the area of iron actually attacked accounts in some measure for the irregularities in the position of points not falling on the straight line in the plot.

The fact that the acceleration action of increased pressure of oxygen may be looked upon as due to an oxygen electrode, has an interesting bearing upon Dunstan's theory of the intermediate formation of hydrogen peroxide. Richarz and Lonnes (*Zeit. Phys. Chem.*, xx., 145) decomposed water saturated with air by passing through it, between platinum electrodes, a current of low electrode density. They found that at the cathode the hydrogen was to a large extent not liberated as such, but that it combined with the dissolved oxygen to form hydrogen peroxide. These are exactly the conditions which obtain upon the cathodic portions of iron undergoing corrosion, except that here we have iron instead of platinum. The appearance of hydrogen peroxide is therefore to be expected, provided it can exist on an iron surface. Dunstan could detect it when zinc corroded, but failed to get a positive reaction in the case of iron. Dunstan explains the generally recognised inhibiting effect of the alkalis, potassium dichromate, &c., by the fact that they all instantly decompose hydrogen peroxide. If some condition already exists upon the surface of the iron such that hydrogen peroxide cannot exist, and if hydrogen peroxide is a step in the formation of rust, it is difficult to see what influence either for or against corrosion substances can have which also destroy hydrogen peroxide. The peroxide, if formed at all, can be formed only when hydrogen is being oxidised by the dissolved oxygen, and the latter reaction takes place, as we have shown, on points separated from the points at which iron is passing into solution, and where if the water is still, rust patches will not form. The formation of hydrogen peroxide must be considered, therefore, incidental to and not necessary for corrosion.

It is a generally known fact that strong solutions of hydrogen peroxide will entirely protect iron from corrosion. If iron be placed in a solution of pure hydrogen peroxide, oxygen is liberated upon its surface, but no rusting occurs. Moody takes this as a positive proof that oxygen alone cannot occasion corrosion. Assuming that hydrogen peroxide is a cathodic product of the action of iron on water, we would expect the presence of this reagent to inhibit the reaction, inasmuch as the law of mass action demands that the formation of a substance be limited by the concentration of that already formed.

Another possible explanation of the protective effect of hydrogen peroxide may be found in the formation of a kind of passive condition analogous to that produced by potassium dichromate, already referred to. Although much has been written upon this interesting subject there is as yet no perfectly satisfactory theory of passivity. We have noted that in the action of iron on water, when the concentration of the hydrogen ions is not sufficiently large to overcome the excess voltage of the iron surface, no action takes place unless a depolarising substance such as dissolved oxygen is present, and then the surface divides itself into zones of different polarity. It may be possible that when iron is placed in a dichromate solution or hydrogen peroxide solution, it absorbs or occludes so dense a film of oxygen upon its surface as to render the entire piece of metal so strongly cathodic that no corrosive action can take place (A. S. Cushman, *Bulletin* No. 30, Office of Public Roads, U.S. Dept. of Agriculture).

When bright iron is heated in the air, oxygen attacks the iron directly, forming a closely adhering layer of oxide even if it be of but microscopic thickness. That oxygen does not unite directly with iron in aqueous rusting is shown by the experiment already referred to with the porous cell, and also by the fact that the rust formed is never adherent to the surface of the iron. The slightest rubbing with the hand produces a clean, bright surface of pure iron. Only when this layer of ferric hydroxide dries on the surface of the iron is an adherent scale produced. Moody (*Proc. Chem. Soc.*, xxiii., 84), in a very recent communication, describes an experiment in which he shows that iron does dissolve before being precipitated as rust. He uses this fact as a further proof that carbon dioxide is essential to rusting. We see ample grounds for concluding that carbon dioxide was absent in the experiments already outlined, and yet the iron surely passed into solution before precipitating.

If a piece of chemically pure iron free from mechanical strains and without evident crystallisation be immersed in the ferroxyl indicator, the positive and negative zones will be apparent after a few moments. There appears to be an unequal concentration of oxygen or segregation of oxygen upon the surface, which cannot be explained by discernible differences in the character of the surface. If the ferroxyl indicator be removed, the surface cleaned by rubbing with a dry towel, and the indicator again applied, the same separation into zones is seen, though in an entirely different configuration. The indicator is apparently a very delicate one and susceptible to changes in equilibrium, which up to the present have not been detected by other means.

Since corrosion is manifestly an electrochemical action, it seemed probable that if two specimens of iron were selected, one of which had proven itself in practice as especially resistant to corrosion, and another which had shown itself to be very susceptible to corrosion, certain differences in the electrochemical behaviour should be discernible. Two sets of such specimens were obtained. The first consisted of two pieces of sheet metal which had been used as culverts in road building, one of which had given way in but a short time, while the other was practically intact. The second set consisted of two strands of wire from a piece of ordinary barbed wire fencing, one of which was badly corroded upon an exposure of but six months, while its neighbour was apparently in its original condition. Nothing is known of the history of the two wires; the good piece of sheet was known to be from an open hearth steel ingot containing but a trace of manganese, and in the heating and rolling of which extra precautions had been taken to prevent segregation. The poor piece was known to be from an ingot of ordinary Bessemer steel.

If corrosion be an electrochemical phenomenon depending upon the formation of an anode portion and a cathode portion and the passage of a current between these two, the rate of this corrosion may be assumed to be proportional to the difference of potential between the two

surfaces. In order to determine whether there was any marked difference in the samples of iron above referred to, in regard to variation in potential between points taken at random over the surface of each, the following method was employed :—In the case of the sheet metal, specimens were machined to an area of about three square inches in the form of a rectangle one inch wide by three inches in length. A block of paraffin one-quarter inch thick was cut to have the same surface as the sheet metal. A number of small holes about one-eighth inch in diameter were drilled in the paraffin and the latter pressed upon the sheet after warming the same. A number of small electrically insulated cells were thus formed, the bottom of each being a definite portion of the surface of the metal. The physical condition of the different pieces of metal experimented with was made as uniform as possible before applying the paraffin block, by polishing each upon a fine, dry sandstone. When any electrolyte, for example, hundredth-normal potassium chloride solution, was placed in these cells, a difference of potential between any two could readily be measured by means of Poggendorff's compensation method. The composition of the cell was Pt-KCl-Fe-Fe-KCl-Pt. In many cases a current of sufficient intensity was set up to rapidly polarise the platinum wire electrodes which were used to complete the circuit from the electrolyte in one cell, through the measuring instrument to the electrolyte in the other cell. In order to eliminate any effect which a difference in the surface of the platinum wires might introduce, these were heated in a Bunsen burner before each measurement. By taking a measurement and then interchanging the platinum wires in the respective cells, no difference in the reading was observed, and therefore the potential found was independent of the platinum. A cell for investigating the samples of wire was made in an analogous way, using a long wooden trough in which the wires were inserted, and forming cells by building up partitions of paraffin at intervals along the length of the wire.

The differences in the average variation of any two cells taken at random over the surface of sheet metal in the one case and the two wires in the other, are very marked, a typical set of readings being shown in the following table, the figures representing differences in potential, expressed in millivolts, between various cells :—

Poor Sheet.			*Good Sheet.*		
I.	II.	III.	I.	II.	III.
− 56	−60	+ 47	− 5	− 5	− 8
+ 48	+21	− 86	0	− 8	0
+ 39	+30	− 48	+ 4	0	−20
− 26	−93	− 69	0	0	−20
+ 56	−31	−177	+18	− 8	0
− 30	+ 8	− 58	+ 2	+ 8	0
+ 21	+81	− 32	0	0	− 5
Corroded Wire.			*Good Wire.*		
+161	+13	− 30	0	+ 2	+ 8
+ 93	−24	+ 38	+ 4	+13	0
+ 21	+13	+ 63	+13	0	+ 4
+ 43	−21	+103	0	0	+13
+ 8	−56	+ 26	+17	+ 4	+ 4
+ 30	−64	− 43	− 8	− 5	− 8
+ 55	−43	+ 47	0	+ 9	0
− 16	−52	+119	− 5	0	0
+ 78	−21	+ 8	− 8	+26	− 5

After measuring the difference of potential as above, the paraffin was in each case removed, a fresh surface obtained and the experiment repeated. No two cells ever reacted alike, but there was always the marked difference between the two pieces of metal indicated above.

It is as yet too early to decide that measurements of this kind indicate the tendency of iron to corrode, but by investigating a large number of specimens of known resistance to corrosion we hope to obtain definite information on this point.

Summary.

We have—

1. Proven again that carbon dioxide is not essential for the corrosion of iron ;
2. Substantiated the work of Whitney and shown that iron does dissolve in pure water in the absence of carbon dioxide and oxygen ;
3. Shown that the primary function of oxygen in the corrosion of iron is in depolarising those cathodic portions of the iron upon which hydrogen tends to precipitate, and that a secondary function is the oxidation of the ferrous iron ion to the ferric form, with its subsequent precipitation as ferric hydroxide ;
4. Shown that the rapidity of corrosion in water is a linear function of the partial pressure of the oxygen in the atmosphere above the water ;
5. Shown that an electric current can pass between bright iron and iron covered with scale, (1) if the concentration of the hydrogen ions be increased by the presence of an acid, or (2) if oxygen or some other depolarising substance be present ;
6. Shown that in certain instances, areas having marked difference in potential exist in far greater number upon the surface of a piece of iron prone to corrosion than upon iron which is resistant to corrosion.

This investigation is being continued, and in a subsequent paper the more practical phases of the subject will be dealt with.

REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS, 1908.*

Since the preparation of our report for 1907, several important determinations of atomic weights have been published. They are, briefly, as follows :—

Nitrogen.—Richards and Forbes have re-determined the ratio between Ag and NO_3, as shown in the composition of silver nitrate (*Journ. Am. Chem. Soc.*, xxix., 808 ; and *Zeit. Anorg. Chem.*, lv., 34). The ratio found, with all corrections applied, is $Ag : NO_3 = 100 : 57{\cdot}479$. Hence, if $Ag = 107{\cdot}930$, $N = 14{\cdot}037$; and if $N = 14{\cdot}008$, $Ag = 107{\cdot}880$. In short, the higher atomic weight hitherto assigned to silver is inconsistent with the lower value for nitrogen as found in several recent investigations.

Sulphur.—Richards and Jones have measured the ratio between Ag_2SO_4 and AgCl (*Journ. Am. Chem. Soc.*, xxix., 826 ; and *Zeit. Anorg. Chem.*, lv., 72). From the data obtained, if $Ag = 107{\cdot}930$, $S = 32{\cdot}113$, a value much higher than that commonly accepted. If $Ag = 107{\cdot}880$, then $S = 32{\cdot}069$, which is near the figure given in our former tables. Additional evidence relative to this constant is much to be desired, for it influences the determination of many other atomic weights, especially those of the rare-earth metals.

Potassium.—From the ratios Ag : KCl and AgCl : KCl, Richards and Staehler find $K = 39{\cdot}114$, when $Ag = 107{\cdot}930$ and $Cl = 35{\cdot}473$ (*Journ. Am. Chem. Soc.*, xxix., 623 ; and *Ber.*, xxxix., 3611). From the corresponding bromide ratios, with $Br = 79{\cdot}953$, Richards and Mueller find $K = 39{\cdot}1143$ and $39{\cdot}1135$ (*Journ. Am. Chem. Soc.*, xxix., 639 ; and *Zeit. Anorg. Chem.*, liii., 423). The final result of both researches is $K = 39{\cdot}114$, a distinct lowering of the constant in question.

Manganese.—Atomic weight re-determined by Baxter and Hines, from analyses of the chloride and bromide (*Journ. Am. Chem. Soc.*, xxviii., 1560 ; and *Zeit. Anorg. Chem.*, li., 202). The mean of their very concordant determinations is $Mn = 54{\cdot}957$, when $Ag = 107{\cdot}930$.

Cobalt.—From new analyses of the chloride, Baxter and Coffin find $Co = 58{\cdot}997$, or 59 in round numbers (*Journ. Am. Chem. Soc.*, xxviii., 1580 ; and *Zeit. Anorg. Chem.*, li., 171). This confirms the earlier determinations by Richards and Baxter.

* From the *Journal of the American Chemical Society*, xxx., No. 1.

International Atomic Weights. (1908).

Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·9
Arsenic	As	75·0
Barium	Ba	137·4
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·96
Cadmium	Cd	112·4
Cæsium	Cs	132·9
Calcium	Ca	40·1
Carbon	C	12·00
Cerium	Ce	140·25
Chlorine	Cl	35·45
Chromium	Cr	52·1
Cobalt	Co	59·0
Columbium	Cb	04
Copper	Cu	63·6
Dysprosium	Dy	162·5
Erbium	Er	166
Europium	Eu	152
Fluorine	F	19·0
Gadolinium	Gd	156
Gallium	Ga	70·0
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	4·0
Hydrogen	H	1·008
Indium	In	115
Iodine	I	126·97
Iridium	Ir	193·0
Iron	Fe	55·9
Krypton	Kr	81·8
Lanthanum	La	138·9
Lead	Pb	206·9
Lithium	Li	7·03
Magnesium	Mg	24·36
Manganese	Mn	55·0
Mercury	Hg	200·0
Molybdenum	Mo	96·0
Neodymium	Nd	143·6
Neon	Ne	20
Nickel	Ni	58·7
Nitrogen	N	14·01
Osmium	Os	191·0
Oxygen	O	16·00
Palladium	Pd	106·5
Phosphorus	P	31·0
Platinum	Pt	194·8
Potassium	K	39·15
Praseodymium	Pr	140·5
Radium	Ra	225
Rhodium	Rh	103·0
Rubidium	Rb	85·5
Ruthenium	Ru	101·7
Samarium	Sa	150·3
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·4
Silver	Ag	107·93
Sodium	Na	23·05
Strontium	Sr	87·6
Sulphur	S	32·06
Tantalum	Ta	181
Tellurium	Te	127·6
Terbium	Tb	159·2
Thallium	Tl	204·1
Thorium	Th	232·5
Thulium	Tm	171
Tin	Sn	119·0
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·5
Vanadium	V	51·2
Xenon	Xe	128
Ytterbium	Yb	173·0
Yttrium	Y	89·0
Zinc	Zn	65·4
Zirconium	Zr	90·6

Indium.—Mathers, from analyses of indium chloride, found In = 114·88 (*Journ. Am. Chem. Soc.*, xxix., 485; and *Ber.*, xl., 1220). From the bromide, In = 114·86. The author recommends the adoption of the rounded-oft value, 114·9, when Ag = 107·93, Cl = 35·473, and Br = 79·953.

Tellurium.—Norris, by twelve concordant reductions of the basic nitrate, $2TeO_2{\cdot}HNO_3$ to TeO_2, found the atomic weight of tellurium to be 127·48, when N = 14·01 (*Journ. Am. Chem. Soc.*, xxviii., 1675). With N = 14·04, Te = 127·64, which is in better agreement with other recent determinations. The true cause of the difference is not clear.

Neodymium.—Holmberg has re-determined the atomic weight of this element by synthesis of the sulphate from the oxide (*Zeit. Anorg. Chem.*, liii., 83). In mean, when S = 32·06, Nd = 144·08. This is higher by 0·48 than the value given in our table.

Dysprosium.—In two series of determinations, based upon the ignition to oxide of the octohydrated sulphate, Urbain and Demenitroux find for the atomic weight of dysprosium, values ranging between 162·29 and 162·75 (*Comptes Rendus*, cxliii., 598). In mean, Dy = 162·53.

Radium.—Mdme. Curie, in a series of three new determinations, has found a more precise value for the atomic weight of radium (*Comptes Rendus*, cxlv., 422; the atomic weight of radium is also under investigation by Thorpe). Working with material more abundant and pure than that formerly analysed, she found Ra = 226·18 when Ag = 107·8 and Cl = 35·4. With Ag = 107·93 and Cl = 35·45, Ra = 226·45. This number is higher than her earlier determination by more than a unit.

From the data here given, and from those cited in previous reports, it is evident that the entire table of atomic weights is in need of revision. The values assigned to K and Na are too high; those given to Cl and S are too low; and these constants affect the determinations of many others. They depend, however, upon the atomic weight of silver, which is probably, but not certainly, as low as 107·88. It is well known that work upon these fundamental constants is now nearing completion in several laboratories, notably under T. W. Richards, W. A. Noyes, and probably other investigators also. Within a few months it should be possible to enter upon a satisfactory revision of the table, a task which would be unsatisfactory if undertaken now. It is true, as Brauner has suggested (*Chemiker Zeitung*, May 11, 1907), that the present table contains inconsistencies, but they are small in amount, and are due to inconsistencies in the original data from which the values are derived. In our next report we hope to recompute the entire table; but meanwhile, awaiting the completion of the researches which we know to be in progress, we prefer to leave the table practically unchanged. A conservative policy seems to be safer than one of haste, and the delay of another year will do no harm. One exception to the rule may, however, be made. Dysprosium, with the atomic weight 162·5, may now be properly added to the list of the chemical elements, and we recommend its insertion in the table.

It is with the deepest regret that we record the loss, by death, in February last, of our distinguished colleague, Professor Moissan. The Chemical Society of Paris has designated Monsieur G. Urbain as his successor upon this Commission.

(Signed)

F. W. Clarke,
W. Ostwald,
T. E. Thorpe,
G. Urbain.

PROCEEDINGS OF SOCIETIES.

SOCIETY OF CHEMICAL INDUSTRY.

Ordinary Meeting, January 6th, 1908.

Dr. J. Lewkowitsch in the Chair.

"*Some Observations on the Keeping Power of Fehling's Solution, together with Notes on the Volumetric Process of Determining Reducing Sugars with it.*" By Francis Watts, C.M.G., D.Sc., F.I.C., and H. A. Tempany, B.Sc., F.I.C. Read by the Honorary Secretary.

The authors point out that, contrary to the commonly expressed ideas, Fehling's solution, or at least Violette's modification of it, is not liable to deteriorate rapidly if kept in the dark, and if access of air is prevented. The solution can thus be kept mixed ready for use for many months, and it is not necessary to keep the stock in the form of two solutions to be mixed as required.

The actual titration is as follows:—Ten cc. of the Violette-Fehling's solution are measured into a small beaker of about 100 to 150 cc. capacity, and to it is added an equal quantity of distilled water. The solution is brought up to boiling-point on a sand-bath, and the reducing sugar solution added from a burette until the blue colour of the liquid is no longer distinctly visible. The end-point of the titration is determined by filtering drops of the solution on a small specially arranged pad of filtering-paper. A sheet of specially toughened filter-paper forms the top layer; this is placed upon two sheets of filter-paper of a rough fairly open type; these layers of filter-paper are then cut into squares of about 1 sq. cm. The liquid to be tested is dropped on the hardened filter-paper and allowed to soak through the three layers; the two upper layers of filter-paper containing all the precipitated cuprous oxide are rejected, and the spot of liquid on the lower one is tested for unreduced copper with ferrocyanide and acetic acid.

As a result of a number of determinations the authors find that, when sucrose is present, each grm. dissolved in 100 cc. of the solution under examination possesses reducing power equal to 0·0033 grm. of invert sugar dissolved in the same volume, and they advocate the use of this factor by way of correction of the amount of invert sugar determined in the presence of known quantities of sucrose. It is shown that in the absence of this correction the amount of invert sugar determined by Fehling's solution, in such cases as that of sugars, may be seriously in error.

"*The Determinations of Small Quantities of Bismuth.*" By Herbert W. Rowell.

A series of results by six chemists showing remarkable variations on the same samples justifies the appearance of the paper. The usual methods of separation and the ammonium carbonate methods in particular are unfavourably criticised, and sources of error are pointed out. Methods of separation suitable for ores, copper, and base bullion are given, which eventually precipitate the bismuth together with various impurities which do not affect the subsequent colorimetric estimation, but aid in the collection of the bismuth. The colour test depends upon the solubility of bismuth iodide in excess of potassium iodide producing a yellow colour; iodine is destroyed by sulphurous acid, and the effect of other metals is nullified by the methods given. The test is very delicate, and the amount of bismuth in copper or base bullion may be determined within five hours. A convenient form of colorimeter suitable for this, copper, Nessler, and similar colour tests, is also described.

Solubility of Graphite in Iron.—Georges Charpy.—The author has determined the solubility of graphite in iron, using different methods; for instance, dissolving in iron graphite previously separated by cooling, or slowly cooling liquid pig-iron, and his results show that the solubility decreases regularly with the temperature, and most probably the solubility in pure iron at 1000° is 1 in 100.—*Comptes Rendus*, cxlv., No. 25.

NOTICES OF BOOKS.

Coal. By James Tonge. London: Archibald Constable and Co., Ltd. 1907.

This volume belongs to the Westminster series of books upon subjects connected with scientific industries which have a special interest for the public. Town Gas, India-rubber, Electric Power, and Traction have already been treated in different volumes, and Coal might be made quite as interesting as any of these. The author has, however, limited the discussion of his subject in such a way as to reduce rather seriously its attractiveness for the average reader. Thus the paleontology of the coal measures is treated fairly fully, and the chapters on fossil botany are copiously illustrated. At the same time, looking at an illustration of a fossil is a very poor substitute for handling the real thing, and any branch of geology is generally found a dry science unless it is supplemented by a large amount of field work, for which the readers of such a book as this would probably have little opportunity. On the other hand, a description of the working of a coal mine would have been a topic which would surely have interested such readers, but the author has altogether neglected mining practice, although he gives a chapter on the preparation of coal for the market. The chapter on the position and importance of the coal fields of the world is necessarily rather full of statistics, but the early parts of the book on the history and occurrence of coal are well written, and will arouse and stimulate the interest.

The Science Year Book, 1908. London: King, Sell, and Olding.

The Science Year Book for 1908 is a diary, directory, and scientific summary combined. It contains useful meteorological and astronomical data for every day in the year, and ample room is allowed for recording personal observations and notes. Short summaries are given of the progress made in 1907 in different branches of science, and biographies of British and American scientific men of note are included. The value of the Year Book is increased by the addition of logarithm tables and tables of gradients and speeds.

Guide de Préparations Organiques. ("Handbook of Organic Preparations.") By Emil Fischer. Translated by H. Decker and G. Dunant. Paris: Gauthier-Villars. 1907.

Professor Emil Fischer's manual of organic preparations is the outcome of many years' experience of the requirements of students, and is one of the best of its size and scope on the subject. It is divided into two parts, the first of which is intended more especially for the use of chemists, while the second contains the descriptions of the methods of preparation of those compounds which are of more interest and importance for doctors and biologists. An excellent selection of substances has been made, and examples are given of practically all the common methods of synthesis of organic compounds. No theoretical explanations are provided, for the author considers that in the laboratory the student's time is fully occupied with the experimental details, and that therefore, before proceeding to the practical work, he should study the theory of the reactions involved, either in the original publications, to which references are frequently given, or else in standard text-books of organic chemistry. The translation has been made from the latest German edition, and the completeness of the directions given and clearness of language employed together make it particularly suitable for the use of students in large laboratories, where the personal supervision of the teacher is necessarily reduced to a minimum.

Traité de Chimie Analytique Qualitative. ("Treatise on Qualitative Analytical Chemistry.") By L. DUPARC and ALFRED MONNIER. Genève: Libraire Kündig. Paris: Félix Alcan. 1908.

THIS text-book of analytical chemistry is very suitable for the use of senior students. The reactions given for each base and acid in the first part are very numerous, and the general properties of every metal, its oxides, hydroxides, and salts, are included. The systematic separation tables give particularly full explanations, and an ingenious scheme showing the solubility of common salts is likely to be useful. In the second edition an introduction deals with the theoretical knowledge which should be possessed by every student of qualitative analysis. This includes a discussion of the atomic theory and the nomenclature and classification of compounds; there is also a chapter on the theory of solutions and chemical equilibria, and an excellent dissertation on the fundamental principles of qualitative analysis is given. The reactions of some organic acids and alkaloids are considered, and one chapter is devoted to the study of the rare earths.

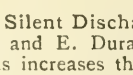
Photographisches Rezept-Taschenbuch. ("Pocket Book of Photographic Recipes.") By P. HANNEKE. Berlin: Gustav Schmidt. 1907.

THIS book is intended both as an instruction book for amateur photographers and a guide for professionals, and gives a short description of most of the best modern methods of preparing negatives and prints. The author has thoroughly tested every recipe given in the book, and hence the beginner may feel confident that he has only to follow implicitly the directions given to get the best possible results with any negative he wishes to develope and print from. The book is issued at a very moderate price, and though it is only of small compass it includes a large number of well-tried recipes. A section on the working up of platinum, silver, and gold residues gives suggestions for such processes as may profitably be applied to these residues on a small scale by the amateur, and general notes on the most suitable preparations and processes to be used for the various operations of developing and fixing, &c., in different cases will be some help to the beginner.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 25, December 16, 1907.

Action of Nitrous Acid upon Allylamine.—Louis Henry.—When subjected to the action of nitrous acid allylamine, $H_2C=CH-CH_2(NH_2)$, unlike propylamine, behaves normally, and gives only the corresponding alcohol. Trimethylene amine,  , the isomer of allylamine, under the same conditions gives allyl alcohol.

Formation of Ozone by the Silent Discharge at a Low Temperature.—E. Briner and E. Durand.—The authors find that cooling the gas increases the yield of ozone. At $-78°$ they obtained 12 grms. of ozone per kilowatt hour. At $-194°$ it is possible to convert the whole of the oxygen into ozone. The most favourable pressure is about 100 mm. of mercury, giving 55 grms. per kilowatt hour. The silent discharge is best for the production of ozone and the spark for nitric oxide.

Certain Relations between the Atomic Weights of Elements.—M. Delauney.—The values of the atomic weights of elements are in the proportion $A^2 : n$, where A and n are whole numbers. Thus (O = 16).

Helium	$2^2 : 1$	Beryllium	$8^2 : 7$
Mercury	$20^2 : 2$	Silicon	$16^2 : 9$
Carbon	$6^2 : 3$	Arsenic	$30^2 : 12$
Potassium	$14^2 : 5$	Bromine	$39^2 : 19$
Molybdenum	$24^2 : 6$		

Moreover, allied elements have either equal divisors, or divisors in regular progression:—

Cadmium	$15^2 : 2$	Cæsium	$61^2 : 28$
Mercury	$20^2 : 2$	Beryllium	$8^2 : 7$
Zinc	$14^2 : 3$	Strontium	$35^2 : 14$
Lithium	$13^2 : 24$	Barium	$62^2 : 28$
Rubidium	$47^2 : 26$		

Elements of the same family have divisors which seem to be regular and symmetrical:—

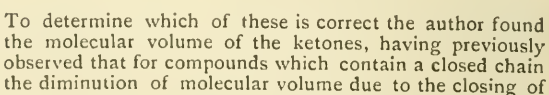
Boron	$11^2 : 11$	Carbon	$12^2 : 12$
Scandium	$23^2 : 12$	Zirconium	$33^2 : 12$
Yttrium	$34^2 : 13$	Silicon	$16^2 : 9$
Lanthanum	$50^2 : 18$	Titanium	$17^2 : 6$
Aluminium	$25^2 : 23$	Cerium	$29^2 : 6$

Fluorine	$19^2 : 19$
Bromine	$39^2 : 19$
Chlorine	$45^2 : 57$
Iodine	$85^2 : 57$

Gases Occluded in Steel.—G. Belloc.—The disengagement of gas is closely connected with the critical points of iron. It is small in the region of α-ferrite, and increases with the temperature. The commencement of the transition of α-into β-ferrite is marked by a copious disengagement which gradually decreases as the transformation proceeds. The disengagement reaches a maximum at the transition of β- into γ-ferrite, and seems to increase with the temperature in the latter region. The gases consist of carbon dioxide and monoxide, hydrogen, and nitrogen. Carbon dioxide is first disengaged and disappears at 550°, when nitrogen appears. From 400° hydrogen and carbon monoxide form the greater part of the gases. The gases were distributed very irregularly throughout the bars of steel investigated.

Extraction of Gases contained in Metals.—O. Boudouard.—The author has performed a series of experiments to study the conditions which allow of the extraction of occluded gases, and he finds that it is extremely difficult to extract all the gases contained in irons and steels. Even when the specimen had previously been twice heated to 1100° the third heating produced a further small quantity of gas, varying from 0·5 per cent of the total volume extracted from the finely-divided metal, to 20 per cent when the metal was in the form of bars and sheets. The quantities of gas extracted are of the order of magnitude of the quantities of sulphur and phosphorus ordinarily found in iron and steel. Incidentally, the author has observed that iron begins to volatilise at 900°.

Constitution of β-Acetoxy-ketones.—E. E. Blaise.—The β-acetoxy-ketones may have either the formula



I. II.

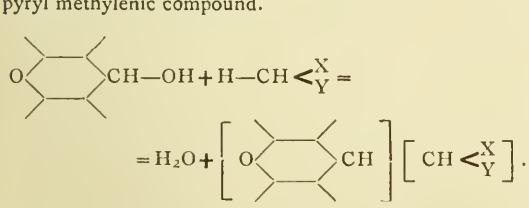
To determine which of these is correct the author found the molecular volume of the ketones, having previously observed that for compounds which contain a closed chain the diminution of molecular volume due to the closing of the chain is very large. The Compound II. would thus have a smaller molecular volume than I. Applying this

method to the ketones he found that the positive or negative variation of volume is of the order of that observed for normal substances with an open chain. Hence these ketones must have the Formula I.

Detection of Tartaric Acid in Cider.—G. A. Le Roy.—The liquid is neutralised, and lead acetate is added in excess. The lead precipitate is washed with cold water and decomposed by sulphuretted hydrogen. The filtered liquid is evaporated and neutralised (after the H_2S has passed off) by means of sodium bicarbonate. It is then evaporated to dryness, and a solution of 1 per cent resorcine in concentrated sulphuric acid is added. On warming, if tartaric acid is present, an intense violet-red coloration is produced. Citric acid gives no coloration; malic and lactic acids give a yellow coloration.

Preparation of Methyl and Ethyl Cyanides.—M. Auger.—Guillemard has recently shown that the formula of potassium cyanide in the solid state is that of the isonitrile. By investigating the action of the aqueous solution of the salt on the neutral sulphates, the acid sulphates, and the iodides of ethyl and methyl, the author has shown that the greater part of the cyanide reacts in the form of K.C:N, but a small part (maximum, 1 per cent) is capable of reacting in the isomeric form and giving carbylamines.

New Reactions of Aromatic Alcohols.—R. Fosse.—The hydroxyl of xanthydrol and of dinaphthopyranol can combine with one atom of the methylenic hydrogen of malonic or cyanacetic acids, β-diketones, β-ketonic esters, and cyanacetic ether, giving one molecule of water and a pyryl methylenic compound.



The hydroxyl of benzhydrol-$p.p$-tetramethyldiamine behaves similarly with the methylenic hydrogen of β-diketones, β-ketonic, and malonic esters. Thus, methylenic tetramethyldiaminobenzhydryl derivatives are obtained. It has never been found possible to replace the hydroxyl in any alcohol by a methylenic residue, $\ldots CH<^{X}_{Y}$. In the aldehydes, on the contrary, the oxygen can easily be replaced by the divalent residue, $:C<^{X}_{Y}$, of malonic, cyanacetic, β-ketonic esters, β-diketones, &c.

No. 26, December 23, 1907.

Influence of Temperature upon the Optical Properties of Dissolved Substances.—C. Chéveneau.—From the results of experiments performed by the author and by Bender, it appears that the variations of the optical constant K for an interval of temperature of about 50° may be calculated from the linear equation $K_{t'} = K_t[1 + m(t' - t)]$, where m is the mean coefficient of cubical expansion of the solution. The general results of the author's investigation are as follows:—1. The index of a dissolved substance varies slightly with the temperature. 2. The variation of the optical constant of a dissolved substance under the influence of the temperature seems to depend upon the change of volume of the solution, and appears to occur in the same sense as the variations in the temperature. 3. The dispersion of the dissolved substance is independent of the temperature to a first approximation.

Determination of Nickel in presence of Cobalt, Iron, and Manganese.—Emm. Pozzi-Escot.—The mineral is treated in such a way that all its metals are dissolved. If metals of the alkaline earths are present they are precipitated by ammonium sulphate. The solution is filtered and concentrated, large excess of a saturated solution of ammonium molybdate is added, and then ammonium chloride solution. The whole is heated to 80° or 90° for some minutes and left to cool for an hour. Thus all the nickel is precipitated as double molybdate of nickel and iron, and nearly all the iron. The solution contains traces of iron, all the manganese, and all the cobalt. It is filtered and the precipitate washed with a saturated solution of ammonium chloride. The precipitate is boiled with water, and ammonium chloride and ammonia are added; thus all the iron is precipitated and all the nickel is left in the filtrate. It may be precipitated by boiling off the ammonia with caustic potash and adding bromine. The oxide is then collected, dissolved in an acid, and the nickel determined by electrolysis.

New Chromium Sulphate.—Paul Nicolardot.—When a solution containing 100 grms. per litre of violet chromium sulphate is boiled, barium carbonate is added, and the liquid filtered, a substance having the formula $(Cr_2O_3)(SO_3)_{2.5}(H_2O)_{7.5}$ is found in the filtrate. This sulphate dissolves easily in water with a slight evolution of heat. The solution is not precipitated by barium chloride nor by sodium phosphate, and thus the substance does not behave either like a sulphate or a salt of chromium. It is precipitated from aqueous solutions by the addition of alcohol or acetone. The aqueous solutions are faintly acid, and are green in colour. As regards the complete repression of the SO_4 ion, this sulphate resembles the green sulphate $(Cr_2O_3)(SO_3)_3(H_2O)_8$ prepared by Recoura.

Influence of Acids and Bases on the Fixation of Acid and Basic Dyes by Wool.—L. Pelet-Jolivet and N. Andersen.—The authors have studied the fixation of crystallised Ponceau and methylene blue by wool in acid, basic, or neutral solution. Their results show that crystallised Ponceau (acid dye) in an acid bath is adsorbed by wool in greater quantities the stronger the acid. In neutral baths only small quantities are fixed, and in alkaline baths none at all. Methylene blue (basic dye) is fixed in smaller quantities the stronger the acid; the fixation is greater in a neutral bath, and at a maximum in an alkaline bath. These facts agree with the colloidal theory of dying. In an acid bath the $\overset{+}{H}$ ions charge the wool positively and increase the fixation of acid ($-ve$) dyes, but decrease that of basic positive dyes. In a neutral bath the wool which is slightly negative fixes more basic than acid dye. In an alkaline bath the $\overset{-}{OH}$ ions charge the wool negatively, and thus the fixation of the positive dye is increased.

Glycide Ethers and Aldehydes in the Naphthalene Series.—Georges Darzens.—α-Naphthylmethyl acetone condenses with ethyl monochloracetate in presence of dry sodium ethylate, giving ethyl-α-naphthylmethyl glycidate, $^{\alpha\text{-}C_{10}H_7}_{CH_3}\!>\!C\!-\!CH\!-\!CO_2C_2H_5$ (with $\backslash O /$). This ether saponifies very easily, giving an acid which decomposes when distilled *in vacuo* into carbon dioxide and α-naphthylmethyl acetic aldehyde, $^{\alpha\text{-}C_{10}H_7}_{CH_3}\!>\!CH\!-\!COH$. The β-naphthylmethyl acetone gives the β-isomer of the same glycide ether.

Isosparteïne.—Charles Moureu and Amand Valeur.—Isosparteïne behaves like a ditertiary saturated base; it does not reduce potassium permanganate in acid solution in the cold. When treated with hydriodic acid by Herzig and Meyer's method it behaves like sparteïne and yields no methyl iodide. It is therefore not methylated at the nitrogen. The molecular refraction of isosparteïne is very close to that of sparteïne, and in general properties the two bases are closely allied.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xl., No. 17, 1907.

Electro-syntheses. — S. M. Losanitsch. — It is a characteristic of the silent electric discharge that it causes the polymerisation or condensation of organic substances, thus synthesising compounds of high molecular weight which probably have a cyclic composition. The products obtained are generally either solid and insoluble, or oily and incapable of being distilled, and hence their purification is a matter of some difficulty. The following results were obtained by the action of the silent discharge :—*Experiments with Sulphur Dioxide.*—$3SO_2 = 2SO_3 + S$, $SO_2 + 2H_2 = 2H_2O + S$, $SO_2 + 2H_2S = 2H_2O + 3S$. *Experiments with Nitric Oxide.* — $4NO = N_2O_4 + N_2$,

$$2NO + 2H_2 = 2H_2O + N_2 = NH_4.NO_2,$$
$$2NO + 2H_2S = 2H_2O + S_2 + 2N,$$
$$2N + 4H_2S = (NH_4)_2S_4.$$

Experiments with Carbon Disulphide.—CS_2 alone gives a brown mass, $(CS_2)_n$. $CS_2 + H$ or H_2S gives an insoluble mass, $3CS_2.2H$. $CS_2 + CO$ gives $3CS_2.2CO$. $CS_2 + C_2H_4$ gives $5CS_2.2C_2H_4$. $CS_2 + C_2H_2$ gives $3CS_2.2C_2H_2$. *Experiments with Acetylene.*—Acetylene condenses and gives two products; one is soluble in alcohol and ether, and remains behind as a thick liquid when its solution is evaporated. The other is a solid, insoluble in all solvents. Analyses of these two products do not agree among themselves, owing to the absorption of the oxygen of the air. Condensed acetylene possesses the property of giving off an emanation which oxidises potassium iodide, liberating iodine, and which acts on the photographic plate through several thicknesses of aluminium or gold foil. It does not ionise the air, and hence is not a radio-active emanation. This action of condensed acetylene is caused by absorbed oxygen, which is bound in a labile state. Acetylene and hydrogen condense, yielding two products of which the one which is soluble has the molecular composition $(C_2H_2.2C_2H_4)_2$, and the same action is observed with acetylene and ethylene, methane, &c. Ethylene by itself and with other organic compounds condenses similarly to substances of high molecular weight.

Amido-group attached to the Nitrogen Atom of Heterocyclic Compounds. — Carl Bülow and Emil Klemann.—The authors have subjected to a thorough examination the N-amido-group of the 1-N-amido-2 . 5-dimethylpyrrol-3 . 4-dicarbonic acid ester described by Bülow in 1902. The most important result of their work is the discovery that while the amido-group attached to the ring carbon of carbo- or heterocylic compounds is readily converted into the diazonium group by the action of sodium nitrite in acid solution, the amido attached to the ring nitrogen under the same conditions is split off as nitrous oxide and is replaced by a hydrogen atom. The N-amido-group of this pyrrol derivative is far less reactive than that of a primary C-amine or of a secondary hydrazine.

Use of the Vacuum for Drying Hydrated Salts.—F. Krafft.—There appears to be no essential difference between the so-called water of crystallisation and of constitution in hydrated salts, although water of constitution escapes exceedingly slowly when these salts are subjected to the vacuum of the cathode light. Since sulphuric acid evaporates rapidly in the vacuum of the cathode light it is not suitable for use as a drying agent, barium oxide being preferable. The author gives the figures he obtained when determining the rate of dehydration of the following salts at different temperatures—zinc sulphate, magnesium sulphate, ferrous sulphate, copper sulphate, calcium sulphate, &c.

Auto-reduction of some Metallic Oxides in the Cathode Light Vacuum, and Volatility of the corresponding Sulphides.—F. Damm and F. Krafft.—Many metallic oxides yield the metal in a vacuum, *e.g.*, lead oxide, bismuth and antimony oxides, especially when the experiments are carried out in tubes of quartz glass. Thus lead oxide at 750° gives a metallic mirror, and small quantities of gas are evolved. Bismuth oxide also undergoes auto-reduction when heated for some hours to 650° in a vacuum. At 1050° the auto-reduction of antimony oxide is very great. Possibly the oxide is converted into a higher oxide, and is then partially reduced as shown by the equation $4Sb_4O_6 = 3Sb_4O_8 + 4Sb$. Then the higher oxide gives up oxygen, again yielding the lower oxide. Thus the oxide can be finally completely reduced. The sulphides of these metals are much more volatile than the oxides, and are therefore more stable on heating. Thus cadmium sulphide volatilises at 770—780°, lead sulphide at 600°, bismuth sulphide at 740°, antimony sulphide at 530°, arsenic sulphide at 230°. This great difference in volatility can be used to separate the sulphides almost quantitatively. Mixtures of sulphur, selenium, and tellurium can also be separated similarly.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, January 28, at three o'clock, Prof. F. J. Haverfield delivers the first of two lectures at the Royal Institution, on "Roman Britain"; on Thursday, January 30, Major Martin Hume commences a course of three lectures on "The Story of the Spanish Armada"; and on Saturday, February 1, Mr. Lionel Cust begins a course of two lectures on "Anthony Van Dyck." The Friday Evening Discourse on January 31 will be delivered by Prof. E. Rutherford on "Recent Researches on Radio-activity"; on February 7, by Mr. Humphry Ward, on "Napoleon and the Louvres"; and on February 14, by Dr. C. W. Saleeby, on "Biology and History." The Discourse on March 13 will be delivered by Chevalier G. Marconi, his subject being "Transatlantic Wireless Telegraphy."

Isomerisation of α-Methyl-sparteïne. — Charles Moureu and Amand Valeur.—The di-iodohydrate of α-methyl-sparteïne when heated to 125° with twice its weight of water in sealed tubes yields the mono-iodomethylate, $C_{15}H_{26}N_2.CH_3I$, of a new base, isosparteïne, which is an isomer of sparteïne. Small quantities of the same substance are produced when the di-iodohydrate of α-methyl-sparteïne is decomposed with alkali, while large yields may be obtained by heating α-methyl-sparteïne on a water-bath with a slight excess of normal sulphuric acid. On neutralising the excess of acid with baryta water and treating with barium iodide, the iodohydrate of the iodomethylate of isosparteïne, $C_{15}H_{26}N_2.CH_3I.HI + H_2O$, is obtained. It decomposes with alkalis, giving the iodomethylate of isosparteïne. The iodohydrate of the iodomethylate of isosparteïne decomposes with heat, giving the iodohydrate of isosparteïne, $C_{15}H_{26}N_2.CH_3I.HI = CH_3I + C_{15}H_{26}N_2.HI$. — *Comptes Rendus*, cxlv., No. 24.

MEETINGS FOR THE WEEK.

Monday, 27th.—Society of Arts, 8. (Cantor Lecture). "Theory and Practice of Clock Making," by H. H. Cunynghame, C.B.

Tuesday, 28th.—Royal Institution, 3. "Roman Britain—(*a*) Its Frontiers and Garrison," by Prof. F. J. Haverfield, M.A., LL.D., &c.

—— Society of Arts, 4.30. "The Development of Colonial Self-Government in the Nineteenth Century," by A. Berriedale Keith, M.A., &c.

Wednesday, 29th.—Society of Arts, 8. "The New Patent Act." by John William Gordon.

—— Society of Dyers and Colourists, 8. "Colloidal Dyestuffs," Dr. E. Feilmann. "Notes on the Dyeing of Celluloid," by Dr. J. N. Goldsmith. General Discussion.

Thursday, 30th.—Royal Institution, 3. "The Story of the Spanish Armada," by Major Martin Hume.

Friday, 31st.—Royal Institution, 9. "Recent Researches on Radio-activity," by Prof. E. Rutherford, F.R.S., &c.

Saturday, Feb. 1st.—Royal Institution, 3. "Anthony Van Dyck," by Lionel Cust, M.V.O., &c.

THE CHEMICAL NEWS.

Vol. XCVII., No. 2514.

THE VARIATIONS OF THE ABSORPTION BANDS OF SALTS OF DIDYMIUM AND ERBIUM IN A MAGNETIC FIELD.

By JEAN BECQUEREL.

It has been observed that under the influence of a low temperature the absorption bands of solids and of solutions become narrower, or are resolved into components. The examination of the spectra of different salts of didymium and erbium, at the temperature of liquid air, has shown that these substances possess many bands which are variable in a magnetic field.

The salt dissolved in an alcohol, or in a mixture of alcohol and water, is contained in a 3 mm. tube inside another tube filled with liquid air, and surrounded by a vacuum. The solidified solution is traversed, between the poles of an electro-magnet, by a beam of light parallel to the magnetic field. By means of a fluor-spar rhombohedron placed before the slit of the spectroscope, and preceded by a quarter-wave plate, it is possible to obtain in the ocular two contiguous regions and to analyse two circular inverse vibrations at once. When the field is excited, the sensitive bands are displaced in opposite directions in the two regions, and the slight ebb and flow which is seen when the direction of the field is reversed several times running, makes it possible to evaluate the order of magnitude of, if not to measure, the very small displacements.

The bands corresponding to circular vibrations in the same sense are not always displaced to the same side; the effect is of the same order of magnitude as the Zeeman effect, even if it is in the reverse sense to that observed for all vapours.

Neodymium Nitrate.—The results obtained with solutions of neodymium nitrate have been described recently. It was found that the sensitiveness of the bands to the action of a magnetic field is independent of the solvent, and it does not appear to be influenced by the addition of a highly magnetic substance (iron perchloride).

The separation of the bands into two components corresponding to inverse circular vibrations can only be obtained in an isotropic substance, or in a uniaxial crystal, the axis of which is oriented parallel to the field; under these conditions, with undissolved neodymium nitrate, only the asymmetric widening and doubling of the very thin bands of the group situated near 625 $\mu\mu$ are seen.

Didymium Chloride.—Didymium chloride in methyl alcohol possesses several variable bands. The most sensitive is the band 509·6 $\mu\mu$ ($+ve$ electrons, displacement 0·11 $\mu\mu$ per 14000 gauss), and it is interesting to observe that in parisite (carbonate of Ce, La, Di, with Ca and F) the most sensitive band is almost in the same place, and is displaced in the same direction and about twice as much.

In the green there is a group, three bands of which are very clear and intense (520·7 $\mu\mu$; 522 $\mu\mu$; 522·5 $\mu\mu$). The band 520·7 $\mu\mu$ ($-ve$ electrons) gives a displacement estimated at 0·04 $\mu\mu$ per 14000; the neighbouring band ($-ve$) is less displaced, and the band 522·5 $\mu\mu$ does not appear to be sensitive.

In the yellow-green group three variable bands are seen; 576·1 $\mu\mu$ ($+ve$, displacement about 0·04 $\mu\mu$), 578·7 $\mu\mu$ ($-ve$), and 579·6 $\mu\mu$ ($-ve$). Finally two strong bands situated near 680 $\mu\mu$ and corresponding to negative electrons give among their components displacements of 0·06 $\mu\mu$ to 0·07 $\mu\mu$.

All these bands are slightly displaced with ethyl alcohol solutions, or in water containing alcohol. Their displacements in a magnetic field seem invariable.

Mixtures of Didymium Choride and Nitrate.—The additions of small quantities of didymium nitrate to a solution of the chloride very rapidly weakens several of the most intense bands (520·7, 522·5, 572·7, 574·5, 576·1 $\mu\mu$); these bands become very faint or disappear in a mixture of 5 parts of chloride and 5 of nitrate in 100 parts of methyl alcohol.

The band 522 $\mu\mu$ persists in the mixture and in the pure nitrate.

In proportion as the amount of nitrate is increased new bands appear (522·9, 523·5, 577·7, 581·4 $\mu\mu$ in a mixture of 7·5 of nitrate, 2·5 of chloride in 100 of methyl alcohol). The band 522·9 $\mu\mu$ (electrons $-ve$, displacement 0·05) steadily increases, and in the pure nitrate is the most intense band of the green group and the most sensitive to the field; the bands 523·5 $\mu\mu$ (electrons $-ve$) and 581·4 $\mu\mu$ (electrons $+ve$), after having passed through a maximum of intensity, also appear, although very much weakened, in the nitrate.

Finally, the addition of water to the alcoholic solution of the nitrate causes the appearance of some bands of the chloride solution, the band 520 $\mu\mu$ in particular.

Thus each of the bands can be followed through its successive transformations; the displacements in a magnetic field always appear to be independent of these transformations.

Didymium Sulphate.—The sulphate being insoluble in a mixture of water and alcohol, widenings and doublings of the fine bands of the orange group (625 $\mu\mu$) were seen in the solid salt, as before in the case of the nitrate.

Oxalate, Fluoride, and other Insoluble Didymium Salts.—The spectra of these salts may be examined by suspending the powdered material in alcohol and solidifying the mass. No band sensitive to the field appeared; probably the bands are not fine enough for the enlargements to be visible.

Erbium Chloride.—The following bands are displaced in a magnetic field:—487 $\mu\mu$ (electrons $-ve$, displacement about 0·1 per 14,000); 488 $\mu\mu$ ($-ve$); 523·8 $\mu\mu$ ($+ve$, displacement 0·08); 541 $\mu\mu$ ($-ve$).

The principal conclusions drawn from these experiments are as follows:—

I. The variability of absorption bands in a magnetic field, which was first observed in the substance possessing the finest bands, xenotime, and then with more difficulty in tysonite, might appear to be an exceptional phenomenon. By the use of low temperatures the first results have been extended to other crystals (parisite, apatite), and then to other solid or dissolved salts. Thus the phenomenon appeared to be general, and it would doubtless be observed in most substances possessing selective absorption, if it were possible to lower the temperature enough to make the bands fine enough. Thermic disturbance seems to be the principal cause of the perturbation of the movements of the absorbing electrons; hence, in order to study the vibrations of the light bands under the best conditions, it is necessary to endeavour to suppress the other movements.

II. In the experiments actually performed the change of period of the corpuscles producing a band seemed to be independent of the temperature as well as of the conditions which more or less modify the band in question. The magnitude of the displacement of a band in a given field seems to be a characteristic property of the oscillating system.

III. The variability of the direction in which the bands corresponding to circular vibrations in the same direction are displaced is a remarkable and unexpected result. After the first observations I suggested the hypothesis either of an inversion of the direction of the field in the interior of certain atoms, or of the existence of positively charged corpuscles. The inversion hypothesis has been supported by many physicists, but it introduces many difficulties, and the invariability of the displacements does not seem to favour this view. I think that it would be premature either to affirm or to deny the existence of positive electrons; it is, however, interesting to notice

that if the magneto-optical phenomena in crystals and salts of the rare earths had been observed before the discovery of radio-activity and of the Zeeman effect, nobody would have had any hesitation in affirming the simultaneous existence of positive and negative electrons possessing masses of the same order of magnitude, when they came to consider these phenomena of the Hall effect.—*Comptes Rendus*, vol. cxlv., 1412.

VOLUMETRIC ESTIMATION OF IRON IN FERRIC COMPOUNDS.

By M. M. PATTISON MUIR.

The process of reducing a ferric to a ferrous compound, by warming with zinc and dilute sulphuric acid, occupies a considerable time; not only must all the iron be reduced to a ferrous compound, but also the whole of the zinc must be dissolved before titration with standard potassium permanganate solution. If very little zinc is put into the liquid, the reduction proceeds very slowly: if much zinc is used, the dissolution of the whole of it takes a somewhat long time.

Mr. Charles Bryant, Senior Laboratory Attendant in the Chemical Laboratory of this College, recently noticed that the reaction between zinc and warm dilute sulphuric acid is stopped by adding an aqueous solution of mercuric chloride—mercury is precipitated on the zinc—and then cooling the liquid.

This reaction may be turned to good account in the volumetric estimation of iron in ferric compounds A measured volume of the solution of the ferric compound is placed in a flask fitted with a cork which carries a glass tube narrowed at its upper end; a fair quantity, say, 200 cc., of dilute pure sulphuric acid and about 20 grms. of granulated zinc, free from iron, are added; the liquid is warmed until there is a brisk evolution of hydrogen, and the flask is shaken from time to time until the reduction is completed. About 100 cc. of a nearly saturated aqueous solution of mercuric chloride are now added; the flask is shaken for three or four minutes, and is then placed under running water until cold. A standard solution of potassium permanganate is now run in until a faint pink colour is obtained in the liquid. When one is estimating iron in solutions containing from 0·005 to 0·01 grm. of ferric iron per cc., and is using 25 cc. of such solutions, an estimation is performed in rather less than half-an-hour. The results of many estimations of iron in ferric compounds, made in this laboratory by the modification of the usual method which has been described, were very satisfactory.

Gonville and Caius College Laboratory, Cambridge.
January 16, 1908.

NEW ZEALAND BONED BEEF.

By ALLISTER MacLEAN WRIGHT.

During the past three or four years New Zealand has exported considerable quantity of beef, boned and packed in boxes lined with parchment paper, then frozen, and shipped in this condition.

This article of food has been exposed to criticism, both as to its quality and its nutritive properties. As the animals, both before and after slaughter, and while being cut up and packed, are under the most rigid inspection by qualified meat inspectors and veterinians appointed by the New Zealand Government, it is impossible for any but healthy animals to be used for this purpose.

No analyses of this meat have yet been published, and from the following analyses, which are typical, it will be seen that the meat contains equal nutritive value with the ordinary flesh of healthy cattle. For comparison, figures given by Mitchell are quoted ("Flesh Foods," p. 47).

The samples were taken from boxes which had been in cold storage for from six to eight weeks, and represent the product as it reaches the market.

It will thus be seen that, with the exception of the cow beef, the composition is practically identical with the flesh of the average cattle beast.

The cow beef contains considerably more fat than the average, but this is a favourable consideration.

	New Zealand boned beef.										Average (Mitchell).		
	Ox.				Cow.			Veal.			Ox.	Cow.	Veal.
	1.	2.	3.	4.	1.	2.	3.	1.	2.	3.	Medium.	Fat.	Lean.
Water	71·08	72·15	70·32	71·13	67·22	62·31	63·14	76·41	77·12	76·28	72·03	70·96	78·82
Nitrogenous substances	21·94	21·37	21·25	21·76	19·68	19·18	18·92	21·81	21·43	21·93	20·96	19·86	19·86
Fat	6·11	5·66	7·58	6·25	12·27	17·70	17·14	1·06	0·77	1·02	5·41	7·70	0·82
Nitrogen-free extractives	—	—	—	—	—	—	—	—	—	—	0·46	0·41	—
Ash	0·87	0·82	0·85	0·86	0·83	0·81	0·80	0·72	0·68	0·77	1·14	1·07	0·50
Nitrogen	3·51	3·42	3·40	3·48	3·15	3·07	3·03	3·49	3·43	3·51	—	—	—
Calculated to Dryness.													
Nitrogenous substances	75·86	76·73	71·60	75·37	60·04	50·88	51·33	92·45	93·66	92·48	74·94	68·39	93·77
Fat	21·13	20·32	25·54	21·65	37·43	46·97	46·50	4·49	31·36	4·30	19·35	26·51	3·87
Nitrogen-free extractives	—	—	—	—	—	—	—	—	—	—	1·64	1·41	—
Ash	3·01	2·95	2·86	2·98	2·53	2·15	2·17	3·06	2·98	3·22	4·07	3·68	2·36
Nitrogen	12·14	12·28	11·46	12·06	9·61	8·10	8·22	14·79	14·99	14·79	12·00	11·13	15·01

In addition, the flesh was examined by the Stas-Gautier method for ptomaines ("Flesh Foods," p. 298), but none could be isolated.

For permission to publish this paper I have to express my thanks to Mr. W. Murray, Manager of the Christchurch Meat Company, Ltd., in whose laboratory most of the work was carried out.

Niobium Sulphide.—Heinrich Biltz and Ludwig Gonder.—The authors prepared very pure niobium pentoxide from sodium niobate, and ignited it in a current of sulphuretted hydrogen. Thus a brown preparation was obtained; it turned white, and evolved sulphur dioxide when heated. Black preparations were obtained when sulphuretted hydrogen and carbon disulphide were led over niobium pentoxide heated to a bright red heat. When these preparations were analysed it was found that they consisted of niobium and sulphur only. However, no formula could be deduced from the analyses, and in all probability pure niobium sulphide has not yet been obtained, the preparations consisting of an unknown sulphide NbS_2 or Nb_2S_5 mixed with niobium or a lower sulphide. No oxysulphide has been prepared.—*Berichte*, 1907, xl., No. 18.

A PHYSICO-CHEMICAL STUDY OF THE COMPLEX COPPER-GLYCOCOLL SULPHATES.*

By J. T. BARKER, B.Sc.

(Concluded from p. 40).

4. *Conductivity Measurements.*

In order to throw further light on the complex formations, measurements of the electrical conductivity of the solutions were carried out. It was expected that on continued addition of glycocoll to copper sulphate solutions a fall of conductivity would be observed, owing partly to the formation of slower moving complex cations and partly to the increased viscosity of the solution, although these effects might be to some small extent counterbalanced by an increased ionisation of the complex sulphate. As will be seen the results obtained are extremely interesting, though they cannot be explained in the manner just indicated.

The copper sulphate used had been re-crystallised three times. The glycocoll (Kahlbaum's) was re-crystallised twice from ordinary distilled water and once from conductivity water ($k = 2 \times 10^{-6}$). The specific conductivity of an $n/10$ solution of this purified glycocoll was 6×10^{-6} (temperature, 25°). It was found that the conductivity of a pure glycocoll solution rises rather rapidly when kept in a conductivity vessel in the presence of the electrodes. This effect is probably due to oxidation at the surface of the platinised electrode. It is interesting to note that it does not occur when $CuSO_4$ is present, so that the complex formation appears to protect the glycocoll from oxidation. The results obtained are given in Table VIII.

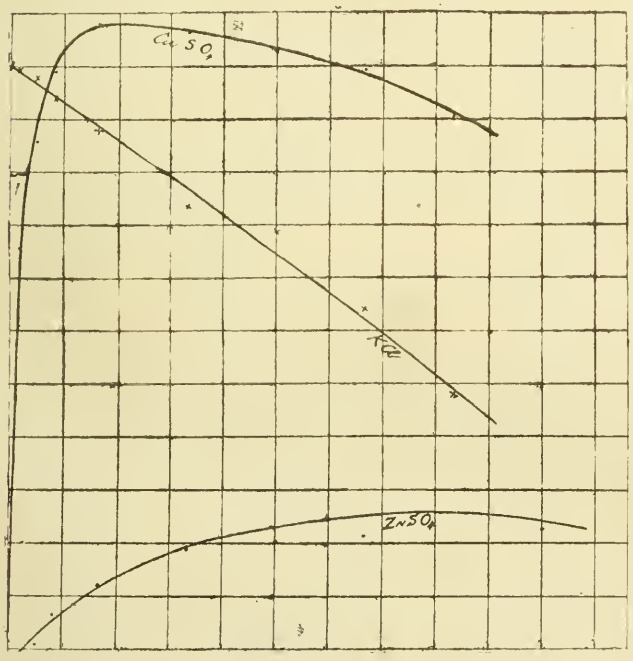


FIG. 1.

The specific conductivities given in Column 2 have been corrected for the specific conductivity of the water (2×10^{-6}).

The curve given in Fig. 1 shows clearly the relationship between conductivity and number of mols. glycocoll present in the solution. In the case of $CuSO_4$ and $ZnSO_4$, the ordinates in the diagram run from 174·7 to 222·7. Contrary to expectation, the first effect of the addition of glycocoll is to increase the conductivity of the solution; thus on the addition of 1 mol. glycocoll the conductivity rises by no less an amount than 16·6 per cent. On the addition of 10 mols. glycocoll per mol. $CuSO_4$ the conductivity attains a maximum (increase of 26·3 per cent), after which further addition of glycocoll produces a gradual decrease of conductivity. The sharp initial rise of conductivity is very marked. In order to see how far this behaviour is to be accounted for by complex formation, the effect of glycocoll on the conductivity of a $ZnSO_4$ solution was studied. The result of these measurements are contained in Table IX.

The zinc sulphate-glycocoll curve, Fig. 1, also shows a maximum, but the effect is not nearly so marked as in the case of $CuSO_4$. Thus on the addition of 1 mol. glycocoll to the $ZnSO_4$ solution the increase of conductivity is only 0·35 per cent, whilst the maximum increase is only 7·3 per cent. With these results may be contrasted the effect of glycocoll on the conductivity of a KCl solution, as shown in Table X.

As will be seen from the curve in Fig. 1, the effect of glycocoll is to diminish the conductivity of the KCl solution by an amount proportional to the concentration of the glycocoll. In the diagram the ordinates for KCl run from 332·52 to 380·52. This diminution is probably due to the increased viscosity of the solution, and is a well known effect of non-electrolytes. This effect will also be present in the cases of $CuSO_4$ and $ZnSO_4$, but there is evidently also present some other cause which tends to *increase* the conductivity, the maxima observed being due to the conflicting action of these two causes. Now both $ZnSO_4$ and $CuSO_4$ are perceptibly hydrolysed in aqueous solution. We may represent the hydrolytic equilibrium by the equation—

$$CuSO_4 + 2H_2O \rightleftarrows Cu(OH)_2 + H_2SO_4$$

or by—

$$Cu^{\cdot\cdot} + 2H_2O \rightleftarrows Cu(OH)_2 + 2H^{\cdot}.$$

Evidently, since glycocoll, being an amphoteric substance, can act both as acid and base, it will disturb this equilibrium. It will tend to remove $Cu(OH)_2$ by the formation of the copper salt of glycocoll, and it may be also supposed to tend to remove $H^{\cdot}$-ions by the formation of glycocoll sulphate. The case of $ZnSO_4$ is similar. Now, it is known that the copper salt of glycocoll is a peculiar salt, which, though the salt of a very weak acid, is preserved from much hydrolysis by an "internal" complex formation (Ley, *Zeit. Elektrochem.*, 1904, x., 954). Hence there may be a considerable formation of this salt from the $Cu(OH)_2$ and the glycocoll, whilst, owing to the fact that glycocoll is a very weak base, there will be only a very small degree of neutralisation of the free acid. The result is that addition of glycocoll to a $CuSO_4$ solution will increase the hydrolysis, producing an increase of $H^{\cdot}$-ions, and hence a considerable increase of conductivity. Somewhat similar considerations will apply to $ZnSO_4$, though in this case, owing to a very much smaller tendency to form complexes, the effect will be much smaller. It is not pretended that these remarks gives a comprehensive analysis of this very interesting equilibrium, though they probably suffice to indicate qualitatively the nature of the reactions occurring. It is necessary, however, to prove that the addition of glycocoll actually *does* increase the $H^{\cdot}$ concentration. Experiments bearing on the point are described in the next section.

* A Paper read before the Faraday Society, December 17, 1907. From the Muspratt Laboratory of Physical and Electro-chemistry. University of Liverpool. Communicated by Dr. F. G. Donnan.

TABLE VIII.—*Conductivity of Glycocoll-copper Sulphate Solutions at 25°. Molar Concentration of* $CuSO_4$ $= n/80$; *Resistance Capacity of Vessel* = 0·3658.

Resistance (ohms).	Specific conductivity of solution (reciprocal ohms per cm. cube).	Mols. glycocoll per mol. $CuSO_4$.
210·12	174·7 × 10⁻⁵	0
179·42	203·7 ,,	1
172·56	211·7 ,,	3
168·44	217·0 ,,	5
165·55	220·7 ,,	10
166·18	219·9 ,,	20
167·25	218·5 ,,	30
168·33	217·1 ,,	40
171·13	213·5 ,,	50

TABLE IX.—*Conductivities of Glycocoll-zinc Sulphate Solutions at 25°. Molar Concentration of* $ZnSO_4 = n/80$; *Resistance Capacity of Vessel* = 0·4226.

Resistance (ohms).	Specific conductivity of solution.	Mols. glycocoll per mol. $ZnSO_4$.
245·40	172·0 × 10⁻⁵	0
244·55	172·6 ,,	1
242·89	173·8 ,,	3
239·82	176·0 ,,	5
236·84	178·2 ,,	10
233·30	180·9 ,,	20
232·58	181·5 ,,	30
231·95	182·0 ,,	40
228·66	184·6 ,,	50
231·36	182·5 ,,	60

TABLE X.—*Conductivities of Glycocoll*-KCl *Solutions at 25°. Molar Concentration of* KCl $= n/40$; *Resistance Capacity* = 0·4005.

Resistance.	Specific conductivity of solution.	Mols. glycocoll per double mol. KCl.
106·30	376·52 × 10⁻⁵	0
106·37	376·27 ,,	1
106·53	375·70 ,,	3
106·98	374·12 ,,	5
107·66	371·76 ,,	10
109·38	365·91 ,,	20
109·94	364·04 ,,	30
111·74	358·18 ,,	40
113·80	351·68 ,,	50

5. *Effect of Glycocoll on the* H· *Concentration of Aqueous Solutions of* $CuSO_4$ *and* $ZnSO_4$.

In order to test whether addition of glycocoll increased the H· concentration of a $ZnSO_4$ solution, the E.M.F. of the cell—

$$Pd H_2 \mid n/80\ ZnSO_4 \mid n/80\ ZnSO_4 + n/8 \text{ glycocoll} \mid Pd H_2$$

(current in direction indicated by arrow)

was measured at 17°, and found to be 0·0052 volt (current in cell in direction indicated by arrow). The palladium electrodes were charged electrolytically to just visible gas-evolution in dilute H_2SO_4, then washed, and left short-circuited in dilute ($n/200$) HCl overnight. They were found to show a small difference of potential when measured against each other in $n/200$ HCl. This has been deducted in the above result.

The E.M.F. of the above cell shows that the addition of glycocoll produces an appreciable increase in the H· concentration. If we neglect the small liquid potential, and calculate by means of the formula $\pi = 0{\cdot}000198\ T \log \frac{C_1}{C_2}$, we find 1·23 as a roughly approximate value for the ratio of increase of the H· concentration. This method cannot be applied to the copper solutions owing to precipitation of metallic copper by the palladium-hydrogen electrode, so in this case comparative measurements on the rate of inversion of cane-sugar were made. The solutions used were 5 per cent with respect to re-crystallised cane-sugar. The polarimeter readings are ive n in the following table. Temperature 60·5° C.

TABLE XI.—*Inversion of Cane-sugar by Copper-glycocoll Solutions.*

Time (minutes)	$n/80$ $CuSO_4$, 5 per cent sugar.	$n/80$ $CuSO_4$, $n/80$ glycocoll, 5 per cent sugar.
0	179° 40′	179° 41½′
70	179° 41′	
66		179° 42′
147	179° 42′	
148		179° 34′
216	179° 41′	
215		179° 30′

These results, though not pretending to great accuracy, are sufficient to show that the presence of the glycocoll has very appreciably increased the H· concentration of the $CuSO_4$ solution.

6. *Products of Isothermal Crystallisation of Aqueous Solutions containing* $CuSO_4$ *and Glycocoll.*

Solutions containing $CuSO_4$ and glycocoll were allowed to crystallise at room temperature over calcium chloride or concentrated sulphuric acid. The crops of crystals so obtained were drained on the filter-pump, dried on porous plates, and then microscopically examined and analysed. Copper was determined electrolytically or as Cu_2S. Glycocoll was calculated from the percentage of nitrogen found on combustion. Water was determined from the loss of weight on heating to 110—120° *in vacuo*, the substance being contained in a weighed glass tube connected with a gas washing flask containing concentrated sulphuric acid. SO_4 was determined gravimetrically in the usual way.

Experiment 1.

Two solutions were made up, each from 12 grms. glycocoll, 5 grms. $CuSO_4.5H_2O$, and 75 cc. water. The first crop of dark blue crystals from each solution was analysed.

	Crystals from Solution 1. Per cent.	Crystals from Solution 2. Per cent.
Copper	10·6	10·37
Glycocoll (by difference)	65·84	68·81
SO_4	18·75	18·01
H_2O	4·81	3·41

For the crop of crystals from Solution 1 we have $\frac{\text{Mols. glycocoll}}{\text{Mols. Cu}} = 5{\cdot}3$. There is more SO_4 present than would, for the given copper content, correspond to $CuSO_4$ or any complex copper-glycocoll sulphate of the formula $Cu(G)_xSO_4$. The amount of water of crystallisation in the crystals from the second solution corresponds pretty closely to 1 mol. water per mol. copper.

If we calculate, taking the figures in the first column, from the Cu percentage the percentages of glycocoll and SO_4 corresponding to the formula $Cu(4G)SO_4.H_2O$, we get 50 and 16 respectively. The excesses over these, namely, 15·84 and 2·75, are in the molar ratio 1·84 : 1. Assuming these crystal crops to be chiefly heterogeneous mixtures of two phases, it seems possible, therefore, that they might consist chiefly of $Cu(4G)SO_4.H_2O$ and $(NH_2—CH_2.COOH)_2H_2SO_4$ (but see later).

Experiment 2.

Solution made up from 18 grms. glycocoll and 10 grms. $CuSO_4.5H_2O$ in 100 cc. water. The first crop of crystals was dried and extracted with ether in a Soxhlet apparatus. The weight of the substance before extraction was 2·2888 grms., after extraction 2·2700 grms. We may conclude therefore that it contains little, if any, free glycocoll. Analysis of extracted crystals :—

Copper	25·23 per cent
Glycocoll	68·29 ,,
SO_4	2·04 ,,
H_2O (by difference)	4·44 ,,

The result of crystallising from a solution relatively richer in $CuSO_4$ (in comparison with glycocoll) is to more than double the copper percentage, whilst the percentage of SO_4 is reduced to one-ninth of its former value. It is evident that this crop of crystals consist mainly of a compound of copper and glycocoll (see discussion of results of Experiment 3).

Experiment 3.

Original solution the same as in Experiment 2. Successive crops of crystals were obtained, examined, and analysed. The crystals were not extracted with ether.

First Crop.—It consisted of dark blue nodular clumps of crystals.

Analysis.

Copper	27·99 per cent
Glycocoll (by difference)	61·88 ,,
SO_4	2·34 ,,
Water	7·79 ,,

Second Crop.—In appearance similar to first crop.

Analysis.

Copper	24·95 per cent
SO_4	3·19 ,,

Other constituents not determined.

Third Crop.—Evidently heterogeneous. It consisted of dark blue needles mixed with almost colourless crystals.

Analysis.

Copper	9·46 per cent
Glycocoll	66·65 ,,
SO_4	19·93 ,,
Water	2·26 ,,

Fourth Crop.—Fairly large colourless crystals, with a small amount of dark blue lumpy solid.

The colourless crystals were free from copper, and contained 30·68 per cent H_2SO_4 (calculated from amount of SO_4 found).

Fifth Crop.—Consisted of a mass of dark blue silky needles, with here and there a small dark blue lumpy nodule.

The blue needles contained 28·47 per cent Cu.

During the course of this work a solution containing glycocoll and $CuSO_4$, which had been set aside to crystallise, became accidentally contaminated with HCl. From this solution large very pale blue (monoclinic or triclinic) crystals were deposited. On analysis they yielded the following results :—

Glycocoll	69·57 per cent
H_2SO_4	30·23 ,,
Copper	0·16 ,,
Water	0·09 ,,

Neglecting the copper and water found, these crystals consist to 99·56 per cent of a sulphate of glycocoll of the composition, glycocoll = 69·66 per cent, H_2SO_4 = 30·34 per cent, which corresponds with the known so-called "basic," glycocoll sulphate, whose formula is $(NH_2.CH_2.CO_2H)_3H_2SO_4$ (glycocoll = 69·87 per cent, H_2SO_4 = 30·13 per cent). These crystals corresponded closely in appearance with the colourless crystals observed in the third and fourth crops (Experiment 3), and from the percentage of H_2SO_4 (30·68) found by analysis in the colourless crystals of the fourth crop, there can be little doubt that these colourless crystals were the "basic" glycocoll sulphate. The dark blue needles observed in the fifth crop were separated as far as possible from the rest by means of a mixture of methylene iodide and benzol. In appearance they closely resembled the well known copper salt of glycocoll, $Cu(NH_2.CH_2.CO_2)_2.H_2O$, and contained 28·47 per cent Cu, whilst copper glycocoll contains 27·7 per cent Cu. There can be little doubt that these two substances are identical.

Judging from the microscopical examination, there was now very strong presumption that the third crop consisted chiefly of copper glycocoll and "basic" glycocoll sulphate. This view is confirmed on examining the following figures :

	I.	II.
Copper	9·46	9·46
Glycocoll	67·93	68·73
H_2SO_4	20·35	20·35
Water	2·26	2·68

Column I. gives the composition of the crop as found by analysis. Now, 9·46 parts Cu as copper glycocoll correspond to 22·01 parts glycocoll and to 2·68 parts water, whilst 20·35 parts H_2SO_4 as $(NH_2.CH_2.COOH)_3H_2SO_4$ correspond to 46·72 parts glycocoll. Therefore, had the crop consisted of copper glycocoll and basic glycocoll sulphate, it would have had the composition indicated in Column II., which agrees sufficiently closely with that given in Column I.

It is impossible to say from the experimental results what are the exact constituents of the first crop of crystals obtained in Experiment 3. It appears possible that they consisted of copper glycocoll admixed with a basic complex copper glycocoll sulphate, but as there is not sufficient other evidence to support such a conclusion, it is scarcely worth while to reproduce here the arithmetical details of the numerous calculations made.

In conclusion, it may be stated that the crystals from Solution 2 (Experiment 1) might be looked upon as mainly a mixture of copper glycocoll and the basic glycocoll sulphate, for on analysis the conglomerate yielded 12·84 per cent N, whilst had it consisted of the substances mentioned, a simple calculation from the other analytical data shows that it would have contained 12·44 per cent N.

7. *Conclusions.*

The crystallisation experiments described in Section 6 confirm the conclusions arrived at in Sections 4 and 5 of this paper, namely, that the effect of the first addition of glycocoll to a solution of $CuSO_4$ is to disturb the hydrolytic equilibrium by the formation of undissociated copper glycocoll, with the consequent increase of free H_2SO_4. The maximum increase in the specific conductivity $n/80$ $CuSO_4$, produced by the addition of 10 mols. glycocoll per mol. $CuSO_4$, was 26·3 per cent. If this $CuSO_4$ solution be regarded (to a first approximation) as completely ionised, then, since the ionic conductivities of $2H\cdot$ and $Cu\cdot\cdot$ are about 2×347 and 80 respectively, the replacement of $Cu\cdot\cdot$ by $2H\cdot$ would increase the specific conductivity by 256 per cent. The actually observed increase would correspond, therefore, to a conversion of only about 10 per cent of the $CuSO_4$ present in the $n/80$ solution into copper glycocoll and free sulphuric acid (which at this dilution would combine with very little glycocoll). It is clear, therefore, that this initial action is soon brought to a stop by the increasing $H\cdot$ concentration (which throws back the $Cu(OH)_2$ concentration), and that after this the further addition of glycocoll results mainly in the formation of complex copper glycocoll cations. This second action, therefore, constitutes the main effect in solutions which contain large excesses of glycocoll relatively to $CuSO_4$. The conclusions arrived at in Sections 1, 2, and 3 remain therefore practically undisturbed. The freezing point measurements alone are sufficient to show that in solutions rich in glycocoll the main actions occurring cannot be represented by the equation—

$$CuSO_4 + 2(NH_2.CH_2CO_2H) = Cu(CO_2.CH_2.NH_2)_2 + H_2SO_4$$

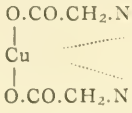
or—

$$CuSO_4 + 4(NH_2.CH_2.CO_2H) = Cu(CO_2.CH_2.(NH_2)_2 + (NH_2.CH_2CO_2H)_2.H_2SO_4;$$

for if so, the addition of 1 mol. of $CuSO_4$ to strong solutions of glycocoll would involve a decided *increase* in the number of "osmotically active" units in the solution, whereas there was always observed a *decrease*. Moreover, the quantitative agreement between the results calculated from

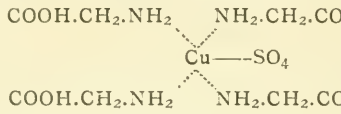
the E.M.F. and freezing point measurements is strong evidence in favour of the theoretical basis on which these results were calculated.

In the complex copper glycocoll sulphates the glycocoll molecules are doubtless related to the copper atom in the same manner as the ammonia molecules in the complex copper ammonia sulphates. In both cases the highest cationic complex appears to contain 4 molecules per 1 atom of copper, and it seems most probable that the glycocoll or ammonia molecules are related to the copper atom through the "subordinate" valencies of the nitrogen atom. The case of copper glycocoll itself has been investigated by Bruni and Fornara (*Rend. d. R. Accad. Lincei*, Roma, xiii., 5a, 26), and by Ley (*Zeit. Elektrochem.*, 1904, x., 954). It appears probable that the constitution of this salt must be represented by the formula—



where the secondary or subordinate valencies are indicated by the dotted lines. The deep colour of all these salts is very striking. It is difficult to resist the conclusion that the powerful selective light absorption which they exhibit is intimately connected with the interplay of these secondary or subordinate affinities, and that this phenomenon is a very general one.

The only way in which one can at present represent the constitution of the complex sulphate $Cu(4G)SO_4$ is therefore (in analogy with the above) as follows :—



in which there exist secondary affinity relationships between the copper and nitrogen atoms.

In conclusion, I have great pleasure in expressing my best thanks to Professor Donnan for his kind advice and assistance during the course of this work.

ON THE OXIDATION OF HYDRAZINE.*

By A. W. BROWNE and F. F. SHETTERLY.

In 1902 Tanatar showed that hydronitric acid could be obtained by treating a molecular mixture of hydrazine sulphate and hydroxylamine chloride in acid solution with certain oxidising agents (*Ber.*, xxxv., 1810—1811). Three years later it was demonstrated in this laboratory that the acid could be prepared by the action of hydrogen peroxide upon hydrazine sulphate in the presence of free sulphuric acid (Browne, *Journ. Am. Chem. Soc.*, 1905, xxvii., 551—555). Still later it was found that by the action of several other oxidising agents, respectively, upon hydrazine sulphate in acid solution, varying amounts of hydronitric acid could be produced (Browne, *Science*, N.S., 1905, xxii., 81). In the present article is described a series of experiments performed for the purpose of ascertaining the conditions under which hydronitric acid is formed by the action of ammonium metavanadate in acid solution upon hydrazine sulphate.

Examination of Materials Employed.—In order to test the purity of the hydrazine sulphate (obtained from Kahlbaum, Berlin) used in these experiments, the percentage of sulphur was determined in six different samples of the material. Found: 24·57, 24·60, 24·56, 24·59, 24·58, and 24·54 per cent; theory, 24·64 per cent.

In the ammonium metavanadate (obtained from E. Merck, Darmstadt) the percentage of vanadium was determined by weighing the pentoxide formed by ignition of a weighed quantity of the original material. Found: 43·23, 43·18, 43·19, and 43·17 per cent; theory, 43·67 per cent. The percentage of nitrogen was determined by distilling the ammonia liberated from a weighed amount of the material in alkaline solution into a measured excess of standard hydrochloric acid. Found: 11·84 and 11·85 per cent; theory, 11·95 per cent.

Preparation of Solutions.—Two solutions of hydrazine sulphate were employed: one containing 15 grms. of the salt per litre, and the other 10 grms. The solution of ammonium metavanadate was prepared in each case by dissolving the proper amount of the salt in a certain measured amount of pure concentrated sulphuric acid and diluting with a measured amount of water after the solution had been cooled to room temperature.

General Procedure followed in the Experiments.—A measured volume of the hydrazine sulphate solution was placed in a distilling flask of about one litre capacity. Through a separatory funnel was introduced a measured volume of the ammonium metavanadate solution. A slow current of air was drawn through the flask in order to carry the hydronitric acid through the condenser into the absorption apparatus. This absorption apparatus consisted essentially of an Erlenmeyer flask (150 cc.) and a Muencke gas wash-bottle. The Erlenmeyer flask was provided with a two-hole stopper through which passed the end of an adapter (connected with the condenser) dipping beneath the surface of the absorbing solution. After passing through the flask the gas was led through a second quantity of the same solution in the Muencke gas wash-bottle.

The absorbing solution was prepared by adding 2 cc. of sodium acetate solution (10 grms. in 100 cc.) and 5 cc. of silver nitrate solution (10 grms. in 100 cc.) to 35 cc. of water. Any hydronitric acid evolved from the reacting mixture was precipitated in the form of silver trinitride. The presence of sodium acetate decreases the solubility of the silver trinitride (Dennis and Isham, *Journ. Am. Chem. Soc.*, 1907, xxix., 18). In every experiment complete absorption of the acid was effected in the Erlenmeyer flask. The yield of hydronitric acid was determined by the method of Dennis and Isham (*loc. cit.*).

Results Obtained in the Experiments.—Four series of experiments were performed in order to ascertain the effect upon the yield of hydronitric acid of varying (1) the temperature at which the reaction is permitted to take place, (2) the amount of metavanadate solution used, (3) the method of introducing the metavanadate solution, and (4) the amount of sulphuric acid present. The results of the different series of experiments are given respectively in Tables I. to IV.

In the sixth column is given for each experiment the highest temperature to which the reacting mixture was heated. As this temperature was raised larger yields of hydronitric acid were obtained. This is at least partially attributable to the fact that the acid formed by the reaction is not completely distilled over into the absorption apparatus unless the temperature is raised to 100°. In these experiments the metavanadate was added at once, with the result that the yield of acid even at 100° was not so high as when the solution was added drop by drop under similar conditions (see Experiment 6).

The most satisfactory procedure was found to be as follows :—The reacting mixture was maintained at a temperature of 80° during the addition of the metavanadate solution. The solution was then brought to the boiling-point, and was held at that temperature for a few minutes in order to effect the complete removal of the hydronitric acid from the mixture. This procedure was followed in all the experiments recorded in Tables II., III., and IV.

In Experiments 7, 8, 9, and 10 the amounts of ammonium metavanadate solution employed correspond to 12, 10, 8, and 6 molecules respectively of the salt for every 3 mole-

* From the *Journal of the American Chemical Society*, xxix., No. 9.

TABLE I.

No. of experiment.	$N_2H_4H_2SO_4$ (100 grms. per litre).		NH_4VO_3 solution. NH_4VO_3 per 100 cc.	NH_4VO_3 solution. Concentrated H_2SO_4 per 100 cc.	Temperature.	AgCl obtained.	Yield NH_3.
	Cc.	Cc.	Grms.	Cc.		Grm.	Per cent.
1.	30	100	1·2709	12·8	20°	0·00345	2·09
2.	30	100	1·2709	12·8	60	0·0049	2·97
3.	20 (*a*)	100	1·2709	12·8	60	0·00485	2·94
4.	30	100	1·2709	12·8	100	0·0126	7·62
5.	30	100	1·2709	12·8	100	0·01215	7·35

TABLE II.

No. of experiment.	$N_2H_4H_2SO_4$ (10 grms. per litre).		NH_4VO_3 solution. NH_4VO_3 per 100 cc.	NH_4VO_3 solution. Concentrated H_2SO_4 per 100 cc.	Method of adding.	AgCl obtained.	Yield NH_3.
	Cc.	Cc.	Grms.	Cc.		Grm.	Per cent.
6.	20 (*a*)	100	1·2709	12·8		0·0207	12·52
7.	30	100	1·0811	12·8		0·01735	10·50
8.	30	100	0·9009	12·8		0·01845	11·16
9.	30	100	0·7205	12·8		0·0166	10·04
10.	30	100	0·5405	12·8		0·0135	8·17

TABLE III.

11.	30	100	1·0811	12·8	At once	0·0135	8·17
7.	30	100	1·0811	12·8	Drop by drop	0·01735	10·50
12.	30	100	1·9009	12·8	At once	0·01055	6·38
8.	30	100	1·9009	12·8	Drop by drop	0·01845	11·16
13.	30	100	0·7207	12·8	At once	0·0135	8·17
9.	30	100	0·7207	12·8	Drop by drop	0·0166	10·04

TABLE IV.

14.	30	100	0·9009	6·4	0·0181	10·95
8.	30	100	0·9009	12·8	0·01845	11·16
15.	30	100	0·9009	19·2	0·0224	13·55
16.	30	100	0·9009	19·2	0·0169	10·23
17.	30	100	0·9009	25·6	0·0200	12·10
18.	30	100	0·9009	38·4	0·01285	7·78
19.	30	100	0·9009	76·8	—	—

TABLE V.

No. of experiment.	Total weight NH_3.	NH_3 formed during reaction.	NH_3 formed.
	Grm.	Grm.	Per cent.
1.	0·09353	0·00174	17·7
2.	0·09327	0·00148	15·1
3.	0·09370	0·00191	19·5
4.	0·09388	0·00209	21·3
5.	0·09179	—	—
6.	0·09179	—	—

(*a*) 15 grms. $N_2H_4H_2SO_4$ per litre.

cules of hydrazine sulphate. In all of these experiments the metavanadate solution was added drop by drop after the hydrazine sulphate solution had been heated to 80°. From these experiments it is apparent that as a general rule the formation of hydronitric acid is facilitated, within certain limits, by increasing the amount of ammonium metavanadate.

In Experiment 11, 12, and 13 the entire quantity of ammonium metavanadate solution was added at the outset. It is obvious that when the solution is added drop by drop the yield of hydronitric acid is materially increased.

From these experiments it appears that when the concentration of sulphuric acid is chosen as indicated for Experiment 15, the maximum yield of hydronitric acid is obtained. In Experiment 16 the metavanadate solution was added more rapidly than in the preceding case, with the result that the yield of the acid was considerably reduced. In all other experiments the solution was added slowly drop by drop.

Identification of the Hydronitric Acid Formed.—The properties of the acid and of its silver salt were studied almost exactly in the manner recommended in a previous article (Browne, *Journ. Am. Chem. Soc.*, 1905, xxvii., 551—555). The percentage of silver in the silver salt was determined with the following results:—(1) 0·21635 grm. of the salt gave 0·20605 grm. of silver chloride; (2) 0·21735 grm. of the salt gave 0·20680 grm. of silver chloride. This corresponds to 71·69 and 71·62 per cent silver (theory, 71·97 per cent), or to 3·4 and 3·05 atoms of nitrogen per atom of silver. For all calculations in the present article the atomic weights recommended by the International Committee for 1907 have been employed.

In order to ascertain whether the amount of ammonia present undergoes increase or decrease during the course of the reaction the series of experiments recorded in Table V. was performed. In Experiments 1, 2, 3, and 4, 50 cc. of ammonium metavanadate solution (containing 12·85 grms. of the salt and 128 cc. of pure concentrated

sulphuric acid per litre) were added slowly to 10 cc. of hydrazine sulphate solution (containing 15 grms. per litre) at a temperature of about 80°. The solution was then made alkaline by the addition of a certain excess of sodium hydroxide solution, and the ammonia was distilled, with the usual precautions, into a measured excess of fifth-normal hydrochloric acid. The amount of ammonia was determined by titrating back with fifth-normal sodium hydroxide solution. In the two blank Experiments 5 and 6, 50 cc. of ammonium metavanadate solution were employed, but no hydrazine sulphate solution.

The amount of ammonia formed in the course of the first four experiments was ascertained in each case by subtracting the total weight of ammonia obtained in Experiment 5 (or 6) from the total weight of ammonia obtained in each of the first four experiments. The percentages of ammonia formed were calculated on the basis of the equation suggested in a subsequent paragraph, and used by the authors in calculating the percentage yields of hydronitric acid.

(To be continued).

THE ATOMIC WEIGHT OF HYDROGEN.*

By WILLIAM A. NOYES.

Some years ago the writer carried out a series of determinations of the quantitative composition of water, from which the value 15·896 was calculated for the atomic weight of oxygen on the hydrogen basis (*Am. Chem. Journ.*, 1890, xii., 441). The opinion was expressed in the paper, that the true value was probably within one part in a thousand of this number, and that it was rather below than above the value reported. Several years later Morley published an account of his elaborate determinations of the densities of hydrogen and oxygen, and of the composition of water by weight, which led him to the value 15·879 for oxygen, or 1·00762 for hydrogen (O = 16) ("Smithsonian Contributions to Knowledge," 1895; *Am. Chem. Journ.*, xvii., 267 and 396; *Zeit. Physik. Chem.*, xvii., 87). Meanwhile Richards had shown that copper oxide retains occluded gases obstinately (*Proc. Amer. Acad.*, 1891, xxvi., 276), a fact which was partly known to me at the time of my work, but which was not as carefully considered as it should have been. There was obtained in each of my experiments, at the end, a small amount of gas which was assumed to be nitrogen on the basis of one or two rather imperfect analyses of the earlier samples. The weight of this gas, calculated as nitrogen, was subtracted from the weight of the hydrogen, giving, on the average, a correction of about one part in a thousand. Several years after the publication of Morley's results it occurred to me that this gas came, very probably, from the copper oxide, and that its weight should be subtracted from the weight of the oxygen instead of from that of the hydrogen. On applying the correction in this manner the value 15·879 (or 1·00765) was found.

While this agreement with Morley's value was gratifying, and the fact was stated to a few personal friends, it did not seem proper to publish a statement about the matter until the surmise could be confirmed by new experimental evidence.

In addition to the desire of confirming or refuting the above explanation of my earlier results, several reasons have made it seem worth while to undertake a new determination of this constant. Hitherto our accurate knowledge of the composition of water has rested on Morley's work alone. He secured so high a degree of concordance in his results, and he exercised such an extraordinary degree of care at every point, that the results obtained by all other observers must be considered as having only confirmatory value in comparison. (This is discussed further in the following paper). It seemed worth while, if possible, to secure a similar order of accuracy by a different method.

Richards and Wells (*Journ. Am. Chem. Soc.*, xxvii., 459) have recently given us a very accurate determination of the ratio between silver and chlorine, but the exact value for the atomic weight of chlorine is still in doubt because the ratio between silver and oxygen is not satisfactorily known (Guye and Ter Gazarian, *Comptes Rendus*, cxliii., 411). A determination of the ratio between hydrogen and chlorine has been carried out at the United States Bureau of Standards, and by using hydrogen generated in the same manner for that determination and for the determination of the composition of water, a very direct comparison between oxygen and chlorine has been secured. As the atomic weights of more than forty elements have been determined in their relation to silver or the halogens, or both, the fundamental importance of the ratios of chlorine and silver to oxygen is apparent.

Finally, it seemed possible to so carry out the work as to secure some evidence with regard to the question of change of weight in a chemical reaction in which a large amount of energy is dissipated. This phase of the problem was

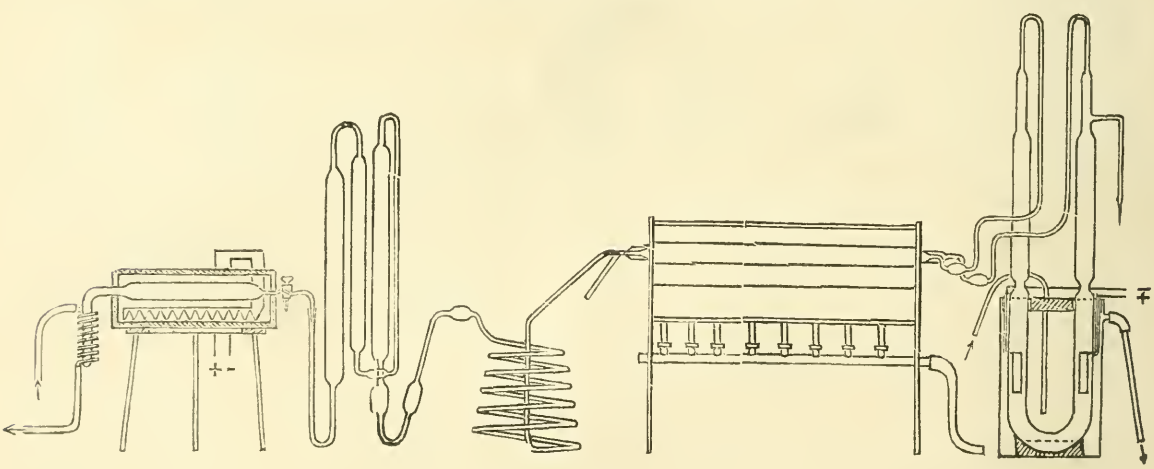


Fig. 1.

* From the *Journal of the American Chemical Society*, xxix., No. 12.

suggested to me while considering the claim made by Prof. S. M. Babcock some years ago that ice loses weight when it melts. He proposed the theory that the loss of weight was intimately connected with the gain of energy by the ice as it melts. If this were true, hydrogen and oxygen should gain weight when they combine to form water. It may be said at once that the results to be given are not conclusive on this point. So far as they have any bearing on the question they indicate a loss rather than a gain in weight when hydrogen is converted into water.

Apparatus.—The apparatus used in the work was, in part, very similar to that used in the previous investigation (*Am. Chem. Journ.*, xii., 441). Five series of determinations have been carried out. In the first four of these the hydrogen and oxygen were obtained by the electrolysis of dilute (15 per cent) sulphuric acid. In the last series the gases were generated by the electrolysis of a 6 to 8 per cent solution of barium hydroxide.

The purifying train will be easily understood from the figure. In the first three series of experiments and in all but the last three determinations of the fourth series, the hydrogen was passed at first through a tube of common glass filled partly with platinised asbestos and partly with copper gauze, and the oxygen was passed through a similar tube filled partly with platinised asbestos, partly with asbestos mixed with lead chromate. These tubes were heated to 300—350°. In the last three experiments of the fourth series hard glass tubes were substituted for the common glass, so that a higher temperature could be used, and in the fifth series hard glass tubes filled with platinised quartz were used. The platinised quartz was prepared by moistening the quartz, which had been heated and quenched in water, with a solution of chlorplatinic acid, and reducing the latter in a current of hydrogen. Each gas then passed through a serpentine tube about 4 metres in length and of 8 mm. internal diameter. These tubes contained a 15 per cent solution of potassium hydroxide, in which was dissolved a small amount of lead oxide. Sulphur compounds present in the hydrogen were reduced to hydrogen sulphide as the mixture passed over the platinised asbestos and copper, and the sulphur of the hydrogen sulphide was retained by the lead as lead sulphide. Only a very small amount of lead sulphide was deposited during the passage of more than 1000 litres of hydrogen through the asbestos. When the barium hydroxide was used as an electrolyte, the serpentine tubes were replaced by bulbs to collect the condensed water, and the solution formed by the deliquescence of the potassium hydroxide. The union between the hard and soft glass was made by grinding the joint and then melting in it a very small amount of Khotinsky cement. Ample evidence is given below that these joints were perfect.

The gases passed next through the tubes containing potassium hydroxide in the form of sticks and then through two or three tubes 15 mm. in diameter and 25 cm. long, filled with phosphorus pentoxide which had been sublimed in a current of oxygen. When not in use these tubes were always sealed, and great care was exercised to avoid the entrance of moist air from the exits where the gases were delivered for use. If the phosphorus pentoxide were to become moist on that side, there would be danger that the gases might carry some of the moisture away with them.

The electrolytic apparatus containing the sulphuric acid or solution of barium hydroxide consisted of a U-tube with platinum electrodes. The limbs of the tube were about 35 mm. in diameter and 55 cm. long. It was filled about two-thirds full at first, and when the solution became too concentrated, water, recently boiled and cooled out of contact with the air, was introduced through the small tube shown on the oxygen side of the apparatus. It was easy to do this without allowing any air to enter, but after each filling a considerable amount of the gases were generated before further use of them for a determination. The water used for preparing the original solution and for subsequent dilutions was purified by re-distilling distilled water with the addition of an alkaline solution of potassium permanganate, and collecting the portion that was free from ammonia.

The resistance of the sulphuric acid in the apparatus was 4 to 5 ohms, while that of the solution of barium hydroxide was considerably greater. It was necessary to cool the electrolytic apparatus with a pretty rapid current of water through the jar containing it. The electrical current used had a pressure of 120 volts, and was reduced by means of a rheostat placed in series with the electrolytic cell. With the sulphuric acid electrolyte a current up to 15 ampéres could be used, giving 6 litres of hydrogen an hour. With the barium hydroxide it was not considered safe to go beyond 4 litres an hour, because of the greater resistance and consequent heating of the solution.

Copper Oxide.—In the first three series of experiments copper oxide was used to convert the hydrogen into water. In the first three experiments copper oxide prepared by precipitating copper sulphate with a hot solution of sodium hydroxide was used. The precipitate was washed by decantation until it became colloidal, and then thoroughly on a Buchner funnel. This oxide retained a trace of sulphate, which was reduced by the hydrogen to sulphur dioxide, and the latter was found in small amount in the water obtained. Only two determinations were made with this oxide. Seven determinations were made with a sample of copper oxide purchased as pure from Kahlbaum. It contained arsenic and other impurities. As these determinations formed a part of the first series, the results of which are rejected for reasons to be given below, they need not be discussed further here. The copper oxide for the remainder of the first, and for the second and third series, was prepared by precipitation of a hot solution of copper sulphate, Rochelle salt, and sodium hydroxide with glucose. The cuprous oxide obtained could be washed indefinitely, and all sulphates were very completely removed. After ignition in a current of oxygen the oxide retained a very small amount of carbon dioxide, but as this appeared as a gas at the end of the experiment, and the amount could be determined, no serious error can have arisen from this source. The same copper oxide was used repeatedly, and after several determinations the carbon dioxide nearly disappeared.

Balance and Weights.—The balance used was made by Ruprecht, of Vienna, and was designed to carry a maximum load of 1 kilogrm. on each pan. The air of the balance case was dried by means of a rapid current of air blown through two wash-bottles containing concentrated sulphuric acid and a little chromic anhydride. The spray of sulphuric acid carried by the current was removed by passing through two tubes, the first containing glass-wool and the second cotton-wool. The current of air was stopped ten to twenty minutes before the weight was determined. During the last series of experiments the balance-case was enclosed in a larger glass case, and the air within the latter was dried by means of large dishes of calcium chloride set on top of the inner case. For determinations in which the weight of the hydrogen was involved, the weight was always determined twice at an interval of one-half hour or more, and with the current of air passing into the case during a part of the interval. In 100 pairs of weights taken from the notebook at random, the average difference was 0·05 mgrm., and the maximum difference 0·12 mgrm.

Weights.—The weights used were carefully calibrated by Mr. Pienkowsky, of the Bureau, at the beginning of the work, a second time after they had been in use for ten months, and a third time at the completion of the investigation, a little more than two years after it was begun. The largest change observed in any of the weights used was 0·04 mgrm.; while none of the platinum weights changed more than 0·01 mgrm. The aluminium rider gained 0·014 mgrm. A re-calculation of the amounts of hydrogen in the last series showed that the use of the new corrections caused no change exceeding 0·14 mgrm. in the weight of the hydrogen for any experiment of that series,

while the algebraic sum of the changes for the five experiments of the series was 0·09 mgrm., or one part in two hundred and fifty thousand of the weight of hydrogen used.

The calibration of the weights was, of course, to a vacuum standard. Since the substances to be weighed were always enclosed in a glass apparatus whose volume remained constant, and which was counterpoised by another glass apparatus of very nearly the same volume and weight, no vacuum correction in the ordinary sense was required. For our present purpose it is most convenient to assume the brass weights in air as standard. If we do this, the platinum weights will appear too heavy because they displace less air in proportion to their weight. This requires a correction of 0·087 mgrm., which must be added for each grm. of platinum weights used. For convenience, a table was prepared which included this correction for the platinum weights with the other corrections as determined in the comparisons of the weights.

(To be continued).

THE CHOICE OF THE MOST PROBABLE VALUE FOR AN ATOMIC WEIGHT: THE ATOMIC WEIGHT OF HYDROGEN.*

By WILLIAM A. NOYES.

A large amount of material has been accumulated from which the atomic weights of the more important elements can be calculated. A very superficial examination of this material reveals the fact that the experimental results on which our knowledge of these constants is based, vary very greatly in their value, and that many of the older determinations have been rendered practically worthless by recent work, which has been more careful and accurate.

As some of these new determinations affect the values for elements of such fundamental importance that a recalculation of the whole table of atomic weights will be necessary in the near future, it seems desirable to formulate some general principles to aid in the elimination of results which have little or no value, and in the combination of the results which remain. Such principles, if they meet with general acceptance, will be of value, not only for the purpose stated, but also as setting a certain standard which must be attained by future workers in this field if their work is to be of permanent value.

The most important general principle which has been proposed for the combination of the results of different observers, is the one based on the mathematical discussion of accidental errors of observation. In accordance with the theory of probabilities, these results, if subject only to accidental errors, should be weighted in inverse proportion to their probable errors (F. W. Clarke, "Constants of Nature," Part V., Edition of 1897, p. 7). A very serious objection to this method of treatment lies in the fact that every determination of this kind is subject to constant errors, and that the amount of these errors is not proportional to their "probable errors" (see Note). Thus Stas obtained 132·8445 ± 0·0008 parts of silver chloride from 100 parts of silver, while Richards and Wells have obtained 132·8670 ± 0·0005 parts (*Journ. Am. Chem. Soc.*, xxvii., 524). The most probable value calculated by the mathematical rule would be 132·8607. If this value is the true one, the real error of the value obtained by Richards and Wells is twelve times its probable error, while the real error of Stas is twenty times the probable error. And, whatever the true value may be, the real error of one of the results, at least, is many times its "probable error." An examination of other cases shows that the relations here found are typical, and it seems evident that the question of constant errors requires some other treatment than the simple mathematical one. The proper treatment, which is an experimental one, has been clearly illustrated in the case which we have under consideration. Richards and Wells studied their method very carefully with especial reference to the elimination of constant errors, and to secure evidence as to the amount of those errors which could not be wholly excluded. They also pointed out certain errors in the work of Stas, and determined, approximately, the magnitude of some of these. It is evident for this reason that very much greater weight attaches to the value found by Richards and Wells than to that found by Stas, and it is proposed as a general principle that when a later observer has pointed out sources of error which are considerable in comparison with the "probable errors," and where the later observer has succeeded in avoiding these sources of error, the earlier work must be looked upon as having only confirmatory value, and the result of the later work should be accepted without modification. It has been objected to this that the later work is also subject to constant errors which may be in the opposite direction from those of the earlier determination, and that if we give a certain weight to the earlier work we may eliminate these errors. But we certainly are not justified in using a value that contains a known error in one direction merely for the chance that we may compensate an unknown error.

(Note.—Professor Clarke has, of course, recognised the importance of constant errors, and has often rejected values which he considers subject to such errors. In 1898 (*Amer. Chem. Journ.*, xx., 543) Prof. T. W. Richards pointed out the importance of selecting atomic weights on the basis of the methods employed in their determination and the probable freedom of those methods from constant errors. It is interesting to notice that of the seven values in Professor Richards' table, which differed at that time decidedly from the values given by Professor Clarke, the numbers for four of the atomic weights are nearer to the numbers now given in the International Table than were the values then given by Professor Clarke).

The principle outlined above has been recently proposed, independently, by Professor Guye in his discussion of the selection of the most probable value for the density of a gas (*Arch. Sci. Phys. Nat.*, xxiv., 44). A second principle proposed by Professor Guye is that when the values obtained by two observers agree while that obtained by a third observer is discordant, the values which are in agreement should be given much greater weight. As an extension of this principle, a value of an individual worker which differs materially from the values obtained by several others, should be rejected entirely.

After eliminating the results which are excluded by the application of the foregoing principles, it is proposed to arrange those which remain in the order of their probable errors. Any result with a probable error more than five times that of the smallest probable error may be excluded, as such a result will have only one twenty-fifth the weight, according to the theory of probabilities. In practical effect, this is the same as using the mathematical rule which Professor Clarke has so long employed in weighting the results of different workers. As at least five or six observations are necessary to give a probable error which has any significance, results based on a smaller number of determinations may be excluded unless other evidence warrants the belief that the work is of an unusual degree of accuracy.

The values for any given ratio which remain after the elimination of results which have little value, may well be combined by weighting them inversely as the squares of their probable errors.

For further use, the ratios which are selected in this manner should be weighted, not by the probable error calculated by the mathematical rule, but by the deviation of the results of different observers from the value selected. If the results of only one observer remain after eliminating untrustworthy values (as in the case of the ratio of silver to silver chloride), this result should be weighted in

* Presented in abstract at the N.Y. Meeting of the American Chemical Society, December 28, 1906.

accordance with the average deviation of the results of this observer from his mean. This will, I think, give a much fairer basis than the "probable error" for weighting the value in such cases. Thus the "mean error" of the value of Richards and Wells given above is 0·0018, while the "probable error" is 0·0005. When we consider the certainty that some sources of constant error will always remain, I think every one will agree that the real error is much more likely to correspond to the former than to the latter value.

After selecting the most trustworthy experimental ratios as suggested, we have still to combine them for the calculation of atomic weights. This may usually be done in a variety of ways. In choosing among these, the same general principles as before should be applied. For a given atomic weight, only those ratios should be used for which the uncertainties of the values will affect the atomic weight chosen less than five times as much as any other combination of ratios which might be used. In most cases this will probably lead to the selection of ratios which furnish a direct comparison with oxygen, silver, or one of the halogens rather than of those in which the comparison is more indirect. Densities of gases corrected to the condition of an ideal gas by the method of D. Berthelot (*Comptes Rendus*, cxliv., 76) may be considered as direct comparisons with oxygen, and molecular and atomic weights calculated from these densities should be included with those determined by chemical methods.

The Atomic Weight of Hydrogen.

The following is a summary of the determinations which have been made of the atomic weight of hydrogen by the chemical method :—

	Date.	No. of expts.	Value.	Prob. error.	Real error.	Real error. / Prob. error.
Dulong and Berzelius .	1821	3	1·00667	356	108	0·3
Leduc.. ..	1892	2	1·00749	83	26	0·3
Erdmann and Marchand.	1842	8	1·00160	71	615	8·7
Thomsen ..	1870	8	1·00570	71	205	2·9
Rayleigh ..	1889	5	1·00692	56	85	1·5
Dumas.. ..	1842	19	1·00250	44	525	12·0
Keiser.. ..	1898	8	1·00753	31	22	0·7
Dittmar and Henderson	1890	24	1·00840	29	65	2·2
Noyes (recalculated) ..	1890	24	1·00765	17	10	0·6
Thomsen ..	1895	21	1·00826	14	51	3·6
Cooke and Richards ..	1887	16	1·00826	13	51	3·9
Noyes (original).. ..	1890	24	1·00654	11	121	11·0
Keiser.. ..	1888	10	1·00306	7	469	67·0
Noyes.. ..	1907	48	1·00787	2	12	6·0
Morley.. ..	1895	23	1·00762	2	12	6·0

The probable errors of the table are calculated from those assigned by Professor Clarke ("Constants of Nature," 1897, Part V., p. 24). For the results of Erdmann and Marchand and Leduc, the values are arbitrary. For convenience these errors are given in units corresponding to the last significant figure of the values for the atomic weights.

On applying the principles which have been outlined, we find that the results of Dulong and Berzelius, Erdmann and Marchand, and of Dumas, are excluded because the later work of Dittmar and Henderson by the same method, demonstrates that serious constant errors were involved in the earlier work. Leduc's value is to be rejected because the number of experiments was too small. Keiser's earlier value is to be rejected because it is not in accord with any of the later work, and because he has himself given us a later and better value. My own original value must be rejected because it was subject to a constant error and the recalculated result may be considered as superseded by my later and more careful work. Because the probable errors of all of the other determinations are more than five times as great as those of Morley and myself, they would be excluded by the third principle proposed. The final value, if calculated from these two results, is 1·00775.

It is interesting to notice the relation between the real errors of the various values (assuming this value as true) and the probable errors. *Only in those cases where we now know that there were serious constant errors, is the real error more than six times the probable error.*

Morley calculates a value corresponding to 1·00762 from his determinations of the densities of the gases and their combining volumes. This value has not been considered here, partly because the probable error of the density of hydrogen is about 3 in 100,000, instead of 2 for the chemical method, but chiefly because of the uncertainty of the ratio of the combining volumes (Morley, "Smithsonian Contribution to Knowledge," 1895, No. 980, p. 110).

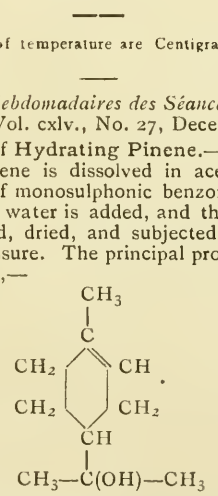
If a value is calculated by Professor Clarke's method, weighting each result in inverse proportion to its probable error, only Keiser's older value and my own original value would affect the value which I have selected by more than about one part in 100,000. Keiser's older value would, however, reduce it by about forty parts, and my own original value by about four parts in 100,000.—*Journal of the American Chemical Society*, vol. xxx., No. 1.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlv., No. 27, December 30, 1907.

New Method of Hydrating Pinene.—Ph. Barbier and V. Grignard.—Pinene is dissolved in acetic acid and an aqueous solution of monosulphonic benzoic acid is added. After twelve hours water is added, and the part insoluble in water is washed, dried, and subjected to rectification under reduced pressure. The principal product is terpineol (melting-point 35°),—



A new hydrocarbon, which the authors are further investigating, is also separated.

Ketone derived from β-Hexahydrocarvacrol.—Leon Brunel.—When β-carvacromenthol, $C_{10}H_{19}OH$, is oxidised by chromic acid in acetic acid solution it is converted into the corresponding ketone, $C_{10}H_{18}O$, carvacromenthone. It is a mobile colourless liquid smelling of cymene. The determination of the physical constants of its derivatives shows that it is identical with the tetrahydrocarvone prepared by Baeyer and Wallach.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xl., No. 18, 1907.

Action of Ozone upon Substances containing a Triple Bond.—C. Harries.—Molinari has stated that ozone can be used to distinguish aliphatic double bonds from aromatic and triple bonds, since it reacts only with those substances which possess an aliphatic structure.

The author, however, finds that this statement is incorrect, and that stearolic acid, for instance, rapidly absorbs ozone and is converted into a typical ozonide. Phenyl propiolic acid also reacts with ozone violently. The splitting of the double bond by means of ozone may be represented by the following scheme :—

$$>C=C<+O_3=>C\underset{\displaystyle O-O}{\overset{\displaystyle |\quad |}{-}}C<+H_2O=>CO+OC<+H_2O_2.$$

$$\backslash\!\backslash\, O\, /\!/$$

and that of the triple bond thus :—

$$-C\equiv C-+O_3=-C\underset{\displaystyle O-O}{\overset{\displaystyle |\quad |}{=}}C-+H_2O=-COOH+HOOC-.$$

$$=O=$$

Rubidium Calcium Sulphates.—J. D'Ans and W. Zeh.—To prepare rubidium syngenite, finely divided gypsum is added to a 30 per cent solution of rubidium sulphate and the mixture allowed to stand in the cold. The salt which separates out is washed with alcohol and ether. Rubidium syngenite crystallises in long needles, and is isomorphous with potassium and ammonium syngenites. A sulphate, $Rb_2Ca_2(SO_4)_3$, separates when 30 per cent rubidium sulphate solution is boiled with gypsum. No rubidium pentacalcium sulphate, $Rb_2Ca_5(SO_4)_6{\cdot}H_2O$, has yet been obtained; if it exists its preparation probably requires a lower temperature and a low $RbSO_4$ concentration.

Some Reactions in Ultra-violet Light.—Herm. Thiele.—The author has performed a series of experiments to investigate the effect of ultra-violet light, using a quartz mercury lamp as a source of light and quartz vessels. With water he obtained no reaction with potassium iodide and starch, but a marked reaction on the addition of ferrous sulphate. Formic acid yielded CO_2, O_2, and CO. Mixtures of CO and O_2 and also of CO and H_2O gave some CO_2. No chlorine (or traces only) was formed from hydrochloric acid.

Porous Materials to Replace Cocks in Working with Gases.—Alfred Stock.—The author describes three modifications of Prytz's apparatus for making an air-tight valve. This apparatus consists of a tube or vessel closed by a porous plate, upon which some mercury is poured. Another tube closed with a similar porous plate (without the mercury) is inserted a short distance in the first. If this second tube is connected with an air-pump and the two porous plates are in contact, air passes through them when the pump is in action; when a sufficient degree of exhaustion is reached, on raising the upper tube with the plate the mercury acts as an air-tight stopper to the lower, and thus the space in the lower tube is closed, so that no air can enter. In Pritz apparatus refractory clay was used for the porous material, but the author has found that a more satisfactory stopper is made by burning a mixture of clay with water-glass and rubber. The material thus obtained is not attacked by boiling water or by dilute acids, and, moreover, it can be fused on to glass. Its porosity is comparatively great.

Action of Silver Nitrate and Mercuric Nitrate upon some Inorganic Hydroxides.—Wilhelm Biltz and Friedrich Zimmermann.—When freshly prepared magnesium hydroxide is moistened with a solution of silver nitrate, the hydrogel is coloured yellowish brown owing to the separation of silver oxide. The authors have studied the action of silver nitrate on the hydroxides of the following metals:—Mg, Zn, Cd, Pb, Be, Al, In, Zr, Sn, Sb, Bi, and find that it is only in the case of the first three that there is any coloration. With mercuric nitrate the hydroxides of Be, Mg, Zn, Cd, Al, Pb, and Mn react. Of the rare earths, La and Nd do not react when heated with silver nitrate, but Pr, Y, Sa, Er give a coloration. All of these react with mercuric nitrate, both in the cold and when heated.

MEETINGS FOR THE WEEK.

Monday, Feb. 3rd.—Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "Nitro-glycerin and its Manufacture," by Lt.-Col. Sir Frederick Nathan and W. Rintoul.
Tuesday, 4th.—Royal Institution, 3. "Roman Britain—(*b*) Its Interior Civilisation," by Prof. F. J. Haverfield, M.A., LL.D., &c.
Thursday, 6th.—Royal Institution, 3. "The Story of the Spanish Armada," by Major Martin Hume.
—— Chemical, 8.30. "The Metallic Picrates," by O. Silberrad and H. A. Phillips. "Organic Derivatives of Silicon Part V., Benzylethylsilicone, Dibenzylsilicone, and other Benzyl- and Benzylethyl Derivatives of Silicane," by R. Robinson and F. S. Kipping. "Some Physico-chemical Properties of Mixtures of Pyridine and Water," by H. Hartley, N. G. Thomas, and M. P. Applebey. "Constitution of Umbellulone," by F. Tutin. "Residual Affinity of the Coumarins and Thiocoumarins as shown by their Additive Compounds," by A. Clayton. "Influence of Foreign Substances on certain Transition Temperatures and the Determination of Molecular Weights," by H. M. Dawson and C. G. Jackson. "Bromination of *p*-Hydroxydiphenylamine," by Miss A. E. Smith and K. J. P. Orton. "Colour and Constitution of *s*-Methine Compounds," by F. G. Pope. "Decomposition of Ammonium Bichromate by Heat," by W. M. Hooton.
Friday, 7th.—Royal Institution, 9. "Napoleon and the Louvre," by Humphry Ward, M.A.
Saturday, 8th.—Royal Institution, 3. "Anthony Van Dyck," by Lionel Cust, M.V.O., &c.

To SOAP MAKERS, CHEMICAL MANUFACTURERS, OIL REFINERS, and OTHERS.—Messrs.

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THE BROMATES OF THE RARE EARTHS.

Part I.—A New Method for the Separation of the Yttrium Earths.

By C. JAMES.

During recent years chemists investigating the rare earths have directed their efforts more towards the cerium group than towards the yttrium earths, with the result that the elements cerium, lanthanum, praseodymium, neodymium, samarium, europium, and gadolinium are fairly well known. On the other hand, the yttrium earths, with the exception of yttrium, ytterbium, and scandium, are still but poorly defined. Many investigators have been of the opinion that "new" erbium is complex, while almost nothing is known about thulium, holmium, dysprosium, and terbium. In addition to the above, victorium, announced by Crookes, is believed by Urbain and some others to be a mixture, although its discoverer still claims that it is a separate and new individual element.

In the case of the cerium group several excellent methods of fractional crystallisation have been developed. On the other hand, no rapid and simple method has been applied to the yttrium earths with the possible exception of the method of Urbain using the ethylsulphates, and some methods employing compounds of a costly nature, such as the acetylacetonates and the metanitrobenzenesulphonates. As one must deal with many kilogrms. of material, expensive compounds are out of the question unless the separation should prove almost quantitative, which is never the case.

Urbain's ethylsulphate method (*Comptes Rendus*, cxxvi., 835; cxxvii., 107; cxxxii., 136) gives good results. He says that yttrium, neo-erbium, and ytterbium accumulate in the most soluble portions, with no trace of the lanthanum group and no earths of the samarium and gadolinium groups. It is very difficult to obtain erbium from fractions rich in holmium by its use, and for separating earths of the same group the method of fusing the nitrates is still the best. Another difficulty is due to the fact that the ethylsulphates are inclined to hydrolyse unless special precautions are taken.

The fractionation of the simple nitrates from concentrated nitric acid proposed by Demarçay (*Comptes Rendus*, cxxii., 728; cxxx., 1020) is very tedious, and the use of a solvent of such a character causes great inconvenience in the laboratory.

The separation obtained by taking advantage of the difference of solubility of the oxalates in a saturated solution of ammonium oxalate developed by Carl Auer von Welsbach (*Monatsh.*, xxvii., 935) gives interesting results. It has drawbacks, however, as it involves the use of two temperatures and requires a large number of operations.

Among the remaining methods only a few need be mentioned:—Fusion of the nitrates and separation of the most easily decomposed portions, by their insolubility in water, separates ytterbium and scandium at one end, and yttrium and terbium at the other. To obtain ytterbium free from erbium and thulium requires about seventy operations. It is also extremely difficult to get yttrium pure by this method, as terbium clings.

Fractional precipitation of the concentrated neutral nitrate solution by means of magnesium oxide (Muthmann and Rolig, *Ber.*, xxxi., 1718), tending to throw down the less basic elements first, gives simllar results.

The precipitation of pure yttria by Muthmann and Böhm's chromate method (*Ber.*, xxxiii., 49, and Chem. News, lxxxi., 169) is comparatively simple, but unfortunately it is of no value for separating the other members.

The fractionation obtained by boiling a solution of the oxalates in ammonium carbonate (*Journ. Am. Chem. Soc.*, xxix., 495, and Chem. News, xcv., 181) works well for obtaining erbium free from holmium and dysprosium on the one side, and thulium, ytterbium, and scandium on the other.

Fractional precipitation to be of value must be very rapid. Fractional crystallisation is to be preferred, for it is much easier to carry out a large number of operations. As a rule, in fractional precipitation methods, especially where dilute solutions are employed, a good deal if not most of the material is washed away. It is highly desirable, therefore, that a method consisting of fractional crystallisation of some type of isomorphous compounds with greatly varying solubilities should be found. With this object in view the author has examined the sulphites, xanthates, succinates, double carbonates with sodium, glycollates, methyl sulphates, normal propyl sulphates, camphorates, iodates, sulphocyanides, sulphocyanide double compounds with mercuric cyanide, monochloracetates, monobromsuccinates, oleates, ferrocyanides, bromates, &c., besides nearly every compound proposed in literature for the purpose of fractionation. The bromates are the best suited for the purpose of all those examined up to the present time.

The bromates are easily prepared by using barium bromate, which in turn is formed by mixing boiling solutions containing the required amounts of barium chloride and potassium bromate. As potassium bromate can be prepared cheaply the rare earth bromates are not costly to obtain.

The rare earth material, generally in the form of the oxalates, is mixed into a paste with sulphuric acid, and the temperature raised until the fumes of sulphuric acid cease to be evolved. The residue is then finely powdered, dissolved in ice cold water, and the resulting solution poured over an excess of barium bromate. This operation is best carried out in a large evaporating dish placed on the water-bath, care being taken to keep the mass well stirred.

After a time the precipitate is allowed to settle, and some of the clear liquid taken up by means of a pipette and added to a warm solution of barium bromate; if no precipitate is obtained the liquid is filtered off. Sometimes, however, a precipitate is formed which consists of barium bromate, and therefore it is best to dilute with water and boil. If the precipitate persists either more stirring or more barium bromate is required.

When the double decomposition is complete a little bromine is often liberated, but there is not sufficient to cause any inconvenience in the laboratory. This is evidently due to the fact that a small amount of bromic acid is formed by the action of a trace of free sulphuric acid accompanying the rare earth sulphates. The latter should therefore be well ignited.

The filtered liquid is evaporated until a drop removed on the end of a glass rod just solidifies when stirred on a watch-glass. Under these conditions just about half of the substance in solution crystallises out on cooling. After a little experience there is absolutely no difficulty in judging the most convenient concentration. If the fractionation is carried out in porcelain dishes a little water should be sprayed on the surface so as to prevent the top from solidifying to a crystalline mass.

Casseroles are by far the best utensils to use for this work, especially if small amounts of substances are being separated, as they can be covered by large watch-glasses. This prevents rapid crystallisation and the tendency of the material to creep up the sides of the vessel. Also there is no need to spray any water on the surface after evaporating or dissolving. Very often, but usually when working with small quantities, the liquid refuses to crystallise, or else the crystals separate out as a fine feathery mass, so that it is quite impossible to pour off the mother-liquor. If it does not crystallise the best procedure is to add a trace of the solid, when the whole immediately solidifies, forming the feathery type of crystal as mentioned above. The

mass is then carefully heated so as to dissolve all but a very little, which will start the crystallisation as the liquid cools. An even better plan is to commence the operation by the addition of a crystal while the liquid is still quite hot.

When working on the large scale very fine hexagonal prisms are often obtained, some being more than two inches in length and over a quarter of an inch in thickness.

Even after six series of crystallisations a considerable change is easily apparent, although this is shown more by the spectroscope than by the colour. The most soluble fraction is very pink, and it gives an intense erbium spectrum. The thulium red is also very strong, and the band in the blue has made its appearance, while the bands of holmium and dysprosium have nearly disappeared. The least soluble fraction is still pinkish, and gives intense dysprosium and holmium bands and a weak erbium spectrum. The colour of the oxide of this fraction is orange, showing that terbium accumulates at this end. After the process has been continued until some twenty fractions have been obtained, the least soluble portion forms brilliant colourless crystals which dissolve in water with a tinge of greenish yellow colour seen only in concentrated solution. The absorption spectrum of this fraction shows very faint samarium and holmium bands, while those of dysprosium are much stronger. Practically the whole of this fraction consists of an earth giving a colourless salt, yttrium. And as the oxide is of a brown ochre colour it shows that terbium collects in the least soluble portion. As one goes down the series the fractions become yellower, and the oxides paler. In the fractions that show the strongest yellow, the dysprosium and holmium bands are very intense, and the oxide becomes yellowish. Farther along the series the lines of erbium make their appearance, and even while the erbium absorption is still weak the liquid assumes a pink colour. This increases until it reaches a rosy pink, at which point the spectroscope shows only erbium bands, and the oxide is of a pure rose tint. Further on still the thulium band in the red shows itself, while the solutions become paler and give a very strong thulium spectrum, the erbium bands becoming decidedly weaker. The most soluble fraction is reached when the solution is nearly colourless; the erbium spectrum is faint, while that of thulium, although fainter, is still intense. The oxide of this last fraction is white and dense, and consists largely of ytterbium.

The above series shows that the rare earth bromates arrange themselves in the following order of solubility:—Samarium (europium ?, gadolinium ?), terbium, yttrium, dysprosium, holmium, erbium, thulium, and ytterbium, which is similar to the solubilities of the oxalates in ammonium oxalate, but different from the ethylsulphates; since, according to Urbain, yttrium, erbium, and ytterbium ethylsulphates are found in the most soluble portion.

A fair conclusion can be drawn that the use of the ethylsulphate method would prove valuable in conjunction with the bromate, especially for the separation of yttrium from dysprosium and holmium, and perhaps for the separation of thulium from ytterbium.

Finally, the author would like to point out some of the rapid separations obtained by this method, the most remarkable being the separation of thulium from erbium. And since ytterbium is still more soluble than thulium its removal is even easier. For example, erbium material, supposed to be quite free from thulium, was converted into the bromate and crystallised four times, when the most soluble portion gave the thulium spectrum.

Dysprosium and holmium also separate from erbium with comparative ease, and as yttrium places itself between terbium and dysprosium the latter element can be obtained terbium free. The division between dysprosium and holmium is not so marked.

The absorption spectra and the colours of the various fractions show curious changes which are not altogether understood, and may be simply due to the comparatively small amount of material under examination.

More material (15 kilos.) is at present being fractionated, and in the near future the less basic portion of earths derived from about 100 kilos. of euxenite and 100 kilos. of yttrotitanite, &c., will also be included. The bromate method will be further investigated and also applied to the cerium group, and the results published at an early date.

New Hampshire College, Durham, N.H.,
November 18, 1907.

EXPERIMENTS ON

THE DECOMPOSITION OF PLATINUM BY AN ALTERNATING CURRENT.

By TH. GROSS.

Potassium carbonate was fused and brought to a yellow-red heat in a platinum crucible, and an alternating current of 50 periods per sec., 120 volts, and 1 ampère was passed for several hours through the molten mass by means of electrodes of strong platinum wire, and at the same time small quantities of potassium nitrate were added. The electrodes and the crucible were gradually consumed, and after some time a deposit of small crystalline needles, resembling graphite in colour, was formed at the electrodes. When the current was interrupted a substance which was insoluble in water was found in the melt, and from it, by washing and drying, a brown powder could be separated. If the loss of weight of the crucible and electrodes amounted to, say, 14 grms., the weight of the powder was 6 grms. It was practically free from potassium and carbon. When it was ignited in hydrogen in a magnesium crucible no platinum could be separated from it. When an unglazed porcelain crucible was used it was decomposed into a metallic substance, crystallising in small needles and resembling platinum, and into another substance which fused to a black glaze with the material of the crucible. Before being heated it was soluble in hot hydrochloric acid, but after ignition it was soluble only in aqua regia. With sulphuretted hydrogen the solution gave a precipitate which, when freshly prepared, dissolved almost entirely in hot yellow ammonium sulphide. By evaporating the filtrate from the sulphuretted hydrogen precipitate a new substance was obtained; this was a light red powder, soluble in hydrochloric acid and precipitated from the solution by excess of caustic potash; it lost weight and became insoluble when ignited, and then could be decomposed by alkalis. It was quite free from platinum. The aqua regia solution of the crystalline needles obtained by electrolysis resembled the brown substance in its behaviour towards sulphuretted hydrogen and ammonium sulphide.

These facts cannot be explained on the supposition that platinum remains undecomposed during the experiment. If the behaviour towards ammonium sulphide of the precipitate obtained by sulphuretted hydrogen were to be explained by assuming the existence of a new modification of platinum, which in the author's opinion is an unjustifiable extension of the conception of a "modification," even then the existence of two new substances with the properties of the brown and red powders would be quite inexplicable. The author therefore assumes that platinum can be decomposed chemically by an alternating current, the following process taking place:—During the electrolysis part of a substance is removed from the platinum, oxidised by the fused alkali, and dissolved. From this oxide the hydrate, a red powder, is formed. The remaining substance, which resembles platinum in appearance, but differs from it in its behaviour towards sulphuretted hydrogen and ammonium sulphide and in other reactions, partly crystallises and is partly oxidised, giving the brown substance. Quantitative experiments were performed to test this assumption. The loss of weight of the crucible and electrodes was determined, and the precipitates obtained by sulphuretted hydrogen from all the products of electrolysis were weighed after being heated in hydrogen.

It was then found that their weight was about 15 per cent less than the loss of weight of crucible and electrodes. It must be noted that platinum with normal properties could not be detected in the substances which had taken part in the electrolysis, but only a substance resembling platinum. It must now be determined how much platinum volatilises during the electrolysis. These observations were confirmed by experiments in which the conducting liquid was fused caustic potash, or a mixture of nitric and sulphuric acids. —*Chemiker Zeitung*, 1907, xxxi., 975.

ON THE OXIDATION OF HYDRAZINE.*

By A. W. BROWNE and F. F. SHETTERLY.

(Concluded from p. 56).

On the Use of Ammonium Metavanadate in the Determination of Hydrazine. — Hofmann and Küspert have recommended the use of ammonium metavanadate in the determination of hydrazine (*Ber.*, 1897, xxxi., 64—67). The procedure followed by these investigators consisted in the slow addition of an excess of ammonium metavanadate solution strongly acidified with sulphuric acid to the hydrazine sulphate lotion. When the evolution of nitrogen (which lasts for about twenty minutes) had ceased, the solution was warmed for several minutes to about 60°. The amount of metavanadate that had been reduced was then determined by titration with permanganate solution. In addition to this volumetric method Hofmann and Küspert also suggested the simultaneous measurement of the nitrogen evolved from the mixture. In effecting this operation the reaction was conducted in a current of carbon dioxide by means of which the evolved nitrogen was carried into the measuring apparatus.

In 1899 Rimini, after reviewing several different methods for the determination of hydrazine, made the statement that the above method was undoubtedly the best of those considered (*Gazz. Chim. Ital.*, 1899, (1), xxix., 265).

The reaction was considered by Hofmann and Küspert to proceed in accordance with the following equation :— $N_2H_4.H_2SO_4 + 2O = N_2 + 2H_2O + H_2SO_4$.

In Experiments 1 to 6 (Tables I. and II.) the authors of the present article have used hydrazine sulphate, ammonium metavanadate, and sulphuric acid in the proportions employed in the experiments of Hofmann and Küspert. In each case appreciable amounts of hydronitric acid were obtained. In Experiment 3 the conditions recommended by Hofmann and Küspert have been exactly duplicated ; the reacting mixture was allowed to stand at room temperature until the effervescence had ceased, when it was heated to 60° for a few minutes. Even under these conditions, unfavourable as they were to the quantitative removal and absorption of the hydronitric acid formed, a yield of nearly 3 per cent was obtained. In Experiment 2 the conditions were the same as in Experiment 3, except that the hydrazine sulphate solution was more dilute. No very appreciable variation in the yield of acid, however, was observed. In Experiments 4 and 5 the yields of hydronitric acid were considerably higher. In Experiment 6 the method of adding the metavanadate solution was modified and the most favourable temperature conditions were chosen. In this case 12·52 per cent of hydronitric acid were produced.

For the sake of simplicity the percentage yields of hydronitric acid and ammonia have both been calculated on the basis of the equation $2N_2H_4 + 2O = HN_3 + NH_3 + 2H_2O$. From the fact, however, that the yields of ammonia under the most favourable conditions were found to be higher than the yields of hydronitric acid, it is apparent that the secondary reaction does not proceed quantitatively in accordance with this equation.

The magnitude of the error introduced as a result of the secondary reaction indicated by the above equation obviously depends upon the character of the analytical method chosen. If the oxidimetric method is employed, the percentage error will be numerically smaller than the percentage yield of hydronitric acid, while if the gasometric method is employed the percentage loss of nitrogen due to the formation of hydronitric acid should be numerically equal to the percentage yield of the acid.

In the four experiments performed by Hofmann and Küspert it was found that one molecule of hydrazine sulphate required 1·996, 1·964, 1·959, and 1·939 atoms of oxygen (theory, 2 atoms). The mean deficit in consumed oxygen (0·0355 atom oxygen per molecule of hydrazine sulphate, or 1·78 per cent deficit in oxygen), corresponds to a yield of 3·55 per cent of hydronitric acid, provided that the absence of possible errors arising from other sources be assumed.

In order to ascertain experimentally the ratio existing between the errors to which the two methods are respectively subject, a series of determinations has been made of the volume of nitrogen liberated and of the amount of oxygen consumed by the oxidation of a measured amount of hydrazine sulphate. In these experiments a Lunge nitrometer was employed, but the ordinary gas evolution bottle was replaced by a 125 cc. Erlenmeyer flask provided with a small test-tube placed in a slanting position. This flask was immersed in a beaker filled with water for the purpose of avoiding errors due to changes in temperature. The hydrazine sulphate and ammonium metavanadate solutions were identical in composition with those employed by Hofmann and Küspert, and the amount of each solution used was also the same as that employed by these investigators (*i.e.*, 10 cc. of hydrazine sulphate solution containing 15 grms. per litre, and 50 cc. of ammonium metavanadate solution containing 12·85 grms. of the salt and 128 cc. of concentrated sulphuric acid per litre were used). After the flask had been brought to room temperature by immersing it in the beaker of water for some time, the two solutions were mixed in the flask, and with frequent shaking were allowed to remain at room temperature until the greater part of the gas had been evolved. The temperature was then raised to 60° for a few minutes, in order to effect the complete evolution of the gas. After the apparatus had been again brought to room temperature, the volume of gas was carefully measured. Since water was used as the confining liquid, corrections for the tension of aqueous vapour were introduced. The amount of oxygen consumed was in each case determined by titration of the residual solution (after diluting to 250 cc.) with a solution of potassium permanganate containing 7·0274 grms. of the salt per litre. Owing to the difficulty in observing the exact end-point of the reaction, a slight excess of permanganate was in each case unavoidably introduced, for which no correction could be satisfactorily made. For this reason the error inherent in the oxidimetric method is to some extent reduced by the compensating error due to the presence of a slight excess of permanganate. The results obtained are given in Table VI.

From the above experiments it is apparent that when the reaction between hydrazine sulphate and ammonium metavanadate in sulphuric acid solution takes place in a Lunge nitrometer, the error due to the formation of hydronitric acid averages about 4·5 per cent in case the gasometric method is employed, or about 1 per cent when the oxidimetric method is used.

Summary.—When hydrazine sulphate and ammonium metavanadate are brought together under favourable conditions in the presence of sulphuric acid, a secondary reaction takes place (to an extent depending on the conditions chosen) which results in the formation of hydronitric acid and ammonia. Under the most favourable conditions studied by the authors the yield of hydronitric acid. as calculated from the equation $2N_2H_4 + 2O = HN_3 + NH_3 + 2H_2O$, amounted to 13·55 per cent of the theory. The highest yield of ammonia

* From the *Journal of the American Chemical Society*, xxix., No. 9.

Table VI.

No. of experiment.	Nitrogen evolved (0°760 mm.).	Deficit in nitrogen.	Permanganate solution.	Oxygen consumed.	Atoms of oxygen per molecule hydrazine.	Deficit in oxygen.
	Cc.	Per cent.	Cc.	Grm.		Per cent.
1.	24·65	4·57	20·4	0·03626	1·966	1·70
2.	24·17	6·43	20·45	0·03635	1·971	1·45
3.	24·61	4·72	20·5	0·03644	1·976	1·20
4.	24·86	3·76	20·7	0·03679	1·995	0·25
5.	24·78	4·07	20·6	0·03661	1·985	0·75
6.	25·02	3·14	20·65	0·03670	1·990	0·50
Average ..	—	4·45	—	—	—	0·975

amounted to 21·3 per cent on the basis of the same equation. The use of ammonium metavanadate in the determination of hydrazine, as recommended by Hofmann and Küspert, is theoretically subject to a percentage error numerically equivalent to the percentage yield of hydronitric acid when the nitrometric method is employed, and to a smaller error when the oxidimetric method is chosen. By the use of a Lunge nitrometer the error was found to be about 4·5 per cent for the nitrometric method and about 1 per cent for the oxidimetric method.

THE ATOMIC WEIGHT OF HYDROGEN.*

By WILLIAM A. NOYES.

(Continued from p. 58).

Purity of the Gases Used.

As with all atomic weight determinations, the value of the present investigation depends in very large measure upon the purity of the substances weighed—in this case, hydrogen, oxygen, and water. The impurities which might be present were :—In the hydrogen, nitrogen, oxygen, water, phosphorus pentoxide, and compounds of sulphur ; in the oxygen, there might be the same impurities with hydrogen in place of oxygen; in the water, sulphur dioxide or carbon dioxide.

Nitrogen.—In the former series of determinations there was obtained at the end of each experiment a small amount of gas which, when calculated as nitrogen, corresponded to about one one-thousandth of the weight of hydrogen used. It was found quite early in the present investigation that when the water is removed from the apparatus containing reduced copper it carries with it a small quantity of hydrogen, probably hydrogen which has been occluded by the copper. The gases were analysed in a narrow eudiometer of such length that when the amount of gas was small, the column of mercury in the eudiometer was 600 to 650 mm. in length, so that the gas was under a pressure of only about one-seventh of an atmosphere. In this way quantities of nitrogen as small as 0·02 mgrm. could be measured.

As will be seen below, it was possible to secure copper oxide so pure that only very small amounts of nitrogen were found at the close of experiments in which it was used. But the best evidence of the freedom of the hydrogen from nitrogen was obtained in the last series. From 22·6 grms. of hydrogen and the equivalent amount of oxygen there was obtained only 0·59 mgrm. of nitrogen. This includes all of the nitrogen in the oxygen as well, and all of the leakage of the stopcock during seven weeks. If we assume that two-thirds of this nitrogen came from the hydrogen, it is only 1 part in 57,000 by weight, or 1 part in 800,000 by volume. On the basis of this evidence it is assumed that all of the hydrogen used was free from nitrogen, and no correction has been made for the small quantities found in each experiment. It is not believed that the error from this source can be so great as 1 part in 20,000.

Incidentally, these experiments have demonstrated the possibility of using, without leakage, ordinary well-ground and carefully lubricated stopcocks under such conditions that they are subjected to atmospheric pressure with a vacuum inside of the apparatus for days together. The well known rubber lubricant was used. It was made by heating a mixture of 16 parts of vaseline, 8 parts of pure rubber, and 1 part of paraffin to a temperature of 350—400° for several hours until it was thoroughly homogeneous. For warm weather, or for a stopcock liable to become warm, a little more paraffin was added.

Oxygen.—After the investigation had progressed so far that it was evident that the results differed from Morley's by a much larger amount than can be accounted for by accidental errors, it was feared that the hydrogen contained a trace of oxygen which escaped conversion into water as the gas passed over the platinised asbestos and copper gauze, especially as the latter were heated to only about 350°. To test this possibility the purified and dried hydrogen was passed through a hard glass tube containing platinised asbestos heated to dull redness, and then through a phosphorus pentoxide tube, The latter was closed with stopcocks, and was weighed each time filled with hydrogen and with the use of a counterpoise. The earlier experiments gave appreciable amounts of water (1 mgrm. from 1 grm. of hydrogen), which was in part, at least, from the asbestos, and even after the asbestos had been heated almost daily for six weeks some water was still obtained (1·1 mgrm. from 2·74 grms. of hydrogen).

(It seems possible that this water may have passed through the walls of the red-hot tube during the five hours of the experiment. It seems not improbable that glass, as a viscous liquid, may dissolve a small amount of water, and that such dissolved water might slowly diffuse through to the inner surface. This question is worthy of further study).

But when some of the same hydrogen was passed over strips of palladium heated to 360° in an electrical air-bath, 3·78 grms. of hydrogen gave a change of weight of −0·08 mgrm. It still seemed possible that a trace of oxygen mixed with *dry* hydrogen might pass the palladium without change. To test this a small T-tube was introduced between the hydrogen generator and the palladium tube in such a manner that the lower arm could be filled with dry oxygen. This would then find its way into the hydrogen by slow diffusion. The amount of oxygen retained in the arm of the T-tube was found in two experiments to be 1·68 and 1·94 mgrms. respectively, while in three experiments in which similar amounts of oxygen were allowed to diffuse into the hydrogen before it entered the palladium tube, there were found 2·29, 2·21, and 2·58 mgrms. of water. While the conditions were such that an exact quantitative agreement could not be expected, the experiments demonstrated that minute quantities of oxygen can be readily detected by this method.

After the close of the last series of experiments the hydrogen was tested by passing it through the tube containing strips of palladium heated to 360°, and then through the pentoxide tube. In these experiments there were passed 2·74, 2·92, and 2·92 grms. of hydrogen respectively, while the changes in weight of the phos-

* From the *Journal of the American Chemical Society*, xxix., No. 1

phorus pentoxide tubes were −0·44, +0·14, and +0·04 mgrms., quantities scarcely beyond the errors of weighing and insignificant in proportion to the weight of the hydrogen.

Water.—The experiments just described demonstrate the absence of water in the hydrogen used in the last series. After the close of the third series, hydrogen from the apparatus was passed through the phosphorus pentoxide tube at the rate of 6 litres an hour for five successive days, 12·6 grms. of hydrogen in all. The changes in weight of the pentoxide tube were −0·01, +0·63, −1·06, −0·33, −0·14 mgrms.; in all a net loss of 0·76 mgrm., or 1 part in 17,000. At the close of the fourth series 3·78 grms. of hydrogen were passed through the pentoxide tube at the rate of 6 litres an hour with a change in weight of −0·04 mgrm., and a similar amount passed through the tubes containing heated palladium gave a change of weight of −0·08 mgrm.

It seems, therefore, that the phosphorus pentoxide used to dry the hydrogen retained its efficiency to the end. The first of these tubes showed considerable deliquescence, caused by the water still remaining in the hydrogen after it passed the sticks of caustic potash, but the last tube showed no sign that it was affected by the moisture.

Phosphorus Pentoxide.—Morley has shown that 1 litre of a gas at ordinary temperatures carries with it only 0·00002 mgrm. of vapour of phosphorus pentoxide (*Journ. Am. Chem. Soc.*, xxvi., 1171). This would correspond to 0·0002 mgrm. in 1 grm. of hydrogen, an amount without any significance in comparison with the degree of accuracy now possible in determinations of atomic weights. It is believed that the crystalline phosphorus pentoxide obtained by sublimation, adhering as it did closely to the walls or the tube and fibres of glass-wool, on which it was deposited, was much less likely to be carried on mechanically by the current of gas than the finely pulverulent pentoxide in its usual form would have been.

Compounds of Sulphur.—After the close of the third series a careful test for compounds of sulphur was made by bringing together the hydrogen and oxygen, delivered by the apparatus, in such a manner that they could be burned and the water collected. The hydrogen was evolved at the rate of 6 litres an hour, the most rapid rate used in the atomic determinations. The water obtained weighed 112·4 grms. A little bromine water and 0·1 grm. of sodium carbonate were added to it, and it was evaporated to dryness in a platinum dish on an electric plate. The residue was acidified with hydrochloric acid, filtered from silica which came from the glass apparatus in which the gases were burned, and the filtrate was tested with a solution of barium chloride. A trifling turbidity appeared slowly, estimated to be less than that occasioned by 0·1 mgrm. of sulphuric acid in a solution of similar volume and character. This would correspond to 1 part of sulphur dioxide, by weight, in 250,000 parts of the hydrogen.

Purity of the Oxygen.—The experiment just described demonstrates the practical absence of sulphur in the oxygen. Tests for moisture also showed that no amount which could be of significance was present.

Purity of the Water.—In the two experiments referred to above in which copper oxide prepared by the precipitation of copper sulphate with sodium hydroxide was used, some sulphur dioxide was found. When pure copper oxide was used no evidence of its presence was ever obtained. In all experiments in which the sulphuric acid electrolyte was used the water was tested with a dilute solution of potassium permanganate (1 cc. = 0·05 mgrm. available O) and with N/10 barium or sodium hydroxide, with phenolphthalein as an indicator. The amounts required never exceeded 0·1 cc. of the permanganate and 0·03 cc. of the N/10 alkali, to produce a colouration in from 20 to 40 cc. of the water. The water of the last two series, especially, was frequently tested for hydrogen peroxide, but none was found.

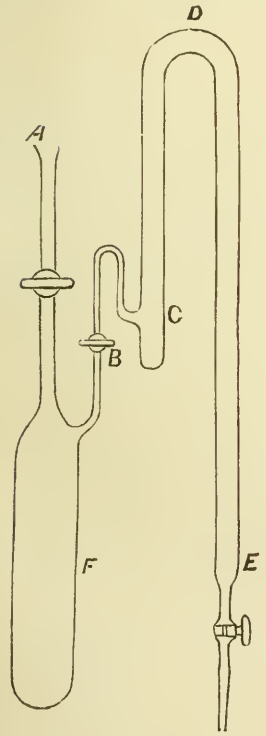


FIG. 2.

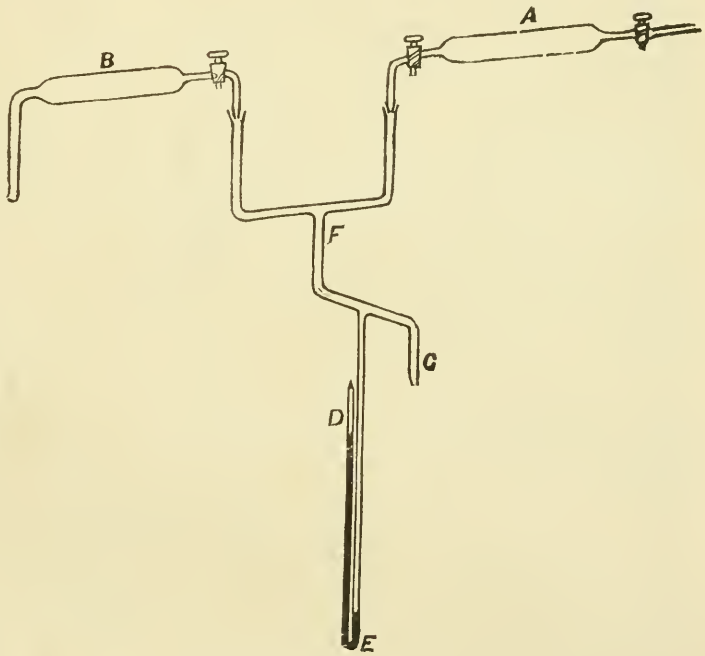


FIG. 3.

First Series.

This series consisted of twenty experiments. In the earlier experiments the weight of the hydrogen was determined by the gain in weight of a piece of apparatus containing copper oxide, the water formed by the oxidation of hydrogen being condensed within the same apparatus. The method used will be clear from Fig. 1. About 160 grms. of copper oxide were placed in the part of the apparatus represented as lying in the electrical air-bath. After sealing the apparatus at the end designed to collect the water, its volume was determined by hydrostatic weighing, and a tube of almost the same volume and weight was prepared. The apparatus was then placed in the air-bath, and heated to 400°, while it was connected with a Sprengel air-pump and exhausted. A phosphorus pentoxide tube, sealed to the pump, was interposed between the pump and the apparatus, and also a small McLeod gauge. The exhaustion was carried to the hundred thousandth of an atmosphere or further, and the heating continued for some time.

(The bulb of the gauge had a capacity of about 16·5 cc. To avoid contaminating the mercury by contact with india-rubber, the gauge was sealed below to an upright glass tube about 12 mm. in diameter. In this was a light, loosely fitting glass plunger. By pressing the plunger down the mercury could be easily forced up into the gauge for the measurement).

For connection with the pump and for other similar connections used throughout the work, the end of the apparatus was drawn out to fit a glass socket connected with the pump. The joint was completed by melting a little Khotinsky cement between the parts in contact. Such a joint, if properly made, will hold for an indefinite length of time against atmospheric pressure, without any leakage that can be measured. The parts are easily separated by gentle warming, and cleaned by warming and wiping with cotton, followed by a cloth moistened with alcohol.

After cooling, the apparatus was rinsed with distilled water, wiped with a clean cloth, and placed on the balance. The tare and weights were placed on the other pan, the current of dry air started through the balance case, and the weighing completed, with the use of the rider, on the following day.

The apparatus was then connected with the source of hydrogen, the copper oxide heated to 300—350°, and hydrogen passed in for four to six hours. A coil of small tin pipe conveying cold water was placed around the part of the apparatus outside of the air-bath to condense the water. By means of the rheostat connected with the electrolytic apparatus it was easy to regulate the supply of hydrogen to correspond with the rate at which it was oxidised by the copper oxide. The operation was always stopped before the copper oxide was all reduced, and by heating for a short time after closing the stopcock, the conversion of the last of the hydrogen to water was completed.

After cooling and standing over night, as before, the weight of the hydrogen, which had been introduced, was determined. The apparatus was then connected at A with the apparatus shown in Fig. 2, the other end, E, of the apparatus being connected with the Sprengel pump. This apparatus was filled with phosphorus pentoxide from C to E. The end at C is designed to collect the phosphoric acid resulting from the deliquescence of the pentoxide, while it is quite necessary that the part C D should be directed up and not down, as otherwise the syrupy phosphoric acid runs down into the unchanged phosphorus pentoxide and seals the tube. The apparatus was, of course, previously exhausted and weighed, using a glass counterpoise of nearly the same volume and weight.

After exhausting the connecting tubes by means of the pump, the bulb F was placed in a freezing mixture of ice and sulphuric acid, the stopcock B was closed, and the stopcock of the copper oxide apparatus opened. By passing hot water through the coil of tin pipe surrounding the part of the apparatus containing the water, the latter was easily distilled into F in the course of two to four hours. By opening B occasionally any permanent gas brought over with the water vapour was allowed to pass on to the pump, and transferred by means of the latter to the eudiometer in which the gas was analysed. When permanent gases were allowed to accumulate in F the passage of the water vapour was checked, and condensation occurred in the connecting tubes. This difficulty occurred especially in the last two series, when considerable hydrogen was present, but was rarely experienced in the first three series. After the water had been transferred to F and the bulb containing the copper had been heated to 400° for a short time, the apparatus containing the water was removed and replaced by a tube containing phosphorus pentoxide, and the heating of the apparatus continued for some time longer. Only a few mgrms. of water were obtained in this manner. The apparatus containing the reduced copper was then cooled and weighed next morning, the loss of weight as compared with the original weight giving the weight of the main portion of the oxygen.

The reduced copper still retains, however, at 400°, either water or hydrogen which cannot be removed by the process described. To obtain this the apparatus was again placed in the electrical air-bath, heated to 400°, and the copper oxidised as far as possible by means of oxygen from the electrical apparatus. The water formed was then removed by connection with a phosphorus pentoxide tube, and heating as before. After cooling and weighing, the apparatus was now ready for a second experiment.

In seven determinations of this series the hydrogen was absorbed in palladium, and its weight was determined twice, first by the loss in weight of the palladium tube, and second by the gain in weight of the copper oxide tube. The palladium tube was given the form shown at A in Fig. 3. The palladium foil was furnished by Heraeus. It was 0·05 mm. in thickness. 360 grms. of it were cut into strips 4 cm. wide, and these were wound in three rolls which were placed in the tube A. Before use the rolls were placed in a hard glass tube, and heated to redness in a current of oxygen. After placing it in A it was heated for some time in a current of hydrogen till thoroughly dry. It was then cooled and charged with hydrogen, and when saturated a current of hydrogen was passed through the tube for a short time. The tube was weighed with a counterpoise, and after standing over night, in the same manner as described for the copper oxide tube.

The arrangement employed for the transfer of the hydrogen to the copper oxide tube is shown in Fig. 3. For greater simplicity the air-baths in which A and B were placed and supported are not shown. The tube C was connected with the Sprengel pump. After exhaustion of the connecting tubes the connection with the pump was cut off by means of a stopcock situated close to the connection with C. The palladium tube was then slowly heated while the copper oxide tube was heated to 350°. The pressure in the system could be easily followed by means of the shortened manometer D E. This contained a small amount of air at D, but not enough to carry the mercury beyond the bend at E when the pressure in F fell to zero. The heating of A was so regulated that the pressure was usually a little below that of the atmosphere, the reaction in B proceeding most rapidly under slightly reduced pressure. The 360 grms. of palladium absorbed 2·3 grms. of hydrogen, and of this 2 grms. could be easily expelled at 150—160°. This amount could be transferred from A to B in three to five hours. The rate of transfer could be followed by the amount of water condensed in B. When enough water had collected, the stopcock of the copper oxide tube was closed, and the palladium was allowed to cool till most of the hydrogen in the connecting tubes had been re-absorbed. The stopcock of the palladium tube was then closed, and the hydrogen in the connecting tubes pumped out into a eudiometer and measured. This

hydrogen varied from 0·02 to 0·14 mgrms. according to the time allowed for the palladium to cool.

The twenty experiments of the first series gave for the atomic weight of hydrogen as calculated from the weight of the hydrogen and the weight of the oxygen, 1·00819 ± 0·00010, and from the weight of the hydrogen and water, 1·00821 ± 0·00010. This is a smaller probable error than has been obtained by any previous observer except Keiser and Morley, but it was found at the close of the series that it is subject to a constant error which is, apparently, about three times the "probable error."

It was known at the beginning of the investigation that copper oxide at 400° would retain a small amount of water. It was hoped, however, that this might be made very small, and also that by making the end of one experiment the beginning of the next the total amount of water retained would be so nearly constant that it would not affect, appreciably, the result of any experiment in the series after the first. At the close of the last experiment of this series it was thought wise to test this point by transferring the copper oxide to a hard glass tube, and heating it in a current of oxygen. To my surprise there was obtained 37·7 mgrms. of water, although the previous oxidation and heating at 400° had given only 3·3 mgrms. If we assume this water to have come from the last six experiments of the series, which formed a continuous set in which the end of one experiment was the beginning of the next, the value for the six determinations becomes 1·00782 as calculated from the hydrogen and oxygen, or 1·00791 as calculated from the hydrogen and water. It was at once decided to reject the determinations thus far made, and which had taken about a year's time, and to begin a new series in which this source of error should be eliminated, if possible.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 16th, 1908.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

MESSRS. F. Buckney, J. E. L. Moore, W. H. Nuttall, and D. Willott were formally admitted Fellows of the Society.

The PRESIDENT announced that the Council had recommended the following gentlemen as Honorary and Foreign Members to be balloted for at the next meeting of the Society:—Messrs. J. A. Le Bel, H. L. Le Chatelier, A. E. J. Gautier, A. Haller, J. W. Hittorf, T. W. Richards, and O. Wallach.

Certificates were read for the first time in favour of Messrs. Robert Barton, jun., 48, Wellclose Mount, Leeds; Harry James Brown, Pembrey Lead Works, Burry Port; Hans Thacher Clarke, Gayton Corner, Harrow; Arnold Merrick, 66, Rothbury Terrace, Newcastle-on-Tyne; Arthur Stead, B.Sc., 113a, Kellner Street, Bloemfontein, O.R.C.; Thomas Marshall Tyson, 2, Osborne Road, Forest Gate, E.; David Thomas Williams, 9, Calvert Terrace, Swansea; Francis Charles Benjamin Wood, Deurne, nr. Antwerp, Belgium.

A certificate was authorised by the Council under By-law I. (3) in favour of Joseph Valentine Francies, Engineering College, Sibpur, Calcutta.

The Council has ordered the following letter and report to be printed in the *Journal* and *Proceedings* of the Society:—

Government Laboratory,
Clement's Inn Passage, Strand, London, W.C.
November 13th, 1907,

GENTLEMEN,—I have the honour to forward you, for presentation to the Council of the Chemical Society, the Report of the International Committee on Atomic Weights, 1908, to which I have appended, as desired by them, the names of Professors Ostwald and Urbain.

It will be seen that since our last Report a number of important re-determinations of atomic weights have been published, and the existing table in consequence reveals a number of small inconsistencies due to the original data from which the values are derived. We think it is inopportune at present to attempt to re-calculate these values as the work known to be in progress on certain fundamental constants, to which reference was made in our last Report, has not yet been published. We have good reason to believe, however, that it will soon make its appearance, and we hope to be able to present an amended table with our Report for next year.—I am, Gentlemen, your obedient Servant, T. E. THORPE.

(The Report was inserted in the CHEMICAL NEWS, January 24th, p. 43).

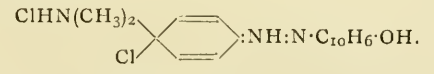
Of the following papers, those marked * were read:—

*1. "*Colour and Constitution of Azo-compounds.* Part II. *The Salts of* p-*Hydroxyazo-compounds with Mineral Acids.*" By JOHN JACOB FOX and JOHN THEODORE HEWITT.

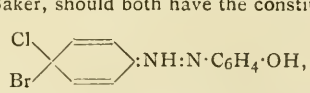
In several communications of one of the present authors, the view has been advanced that, whilst *p*-hydroxyazobenzene has a constitution which is correctly expressed by its name, the salts which it forms with mineral acids are derived from the tautomeric quinonehydrazone. W. B. Tuck (*Trans.*, 1907, xci., 449), from a consideration of the absorption spectra of benzeneazophenol and its ethyl ether in alcoholic and concentrated hydrochloric acid solutions, concludes that the hydrochlorides of both compounds "have similar structures, and consequently the hydrochlorides of the free hydroxyl substances have an azo-structure."

From an examination of benzeneazo-*α*-naphthol and its ethyl ether, the present authors agree with Tuck's statement as to similarity of structure, but deny that this structure is of azo-type, as the reactions of hydroxyazo-compounds in concentrated acid solution negative this view.

F. Baker's attempt (*Trans.*, 1907, xci., 1490) to formulate these compounds as carbonium salts is unsatisfactory; it requires quinquivalent nitrogen in a hitherto unobserved form, whilst the dihydrochloride of dimethylaminobenzeneazo-*α*-naphthol (prepared by the authors) would have to be written—



The most conclusive evidence is given by the fact that the hydrochloride of *p*-bromobenzeneazophenol and the hydrobromide of *p*-chlorobenzeneazophenol, which, according to Baker, should both have the constitution—



are actually different substances, yielding the components from which they are respectively derived when decomposed by alkali.

The present authors suggest, instead of the formulæ hitherto proposed, the constitution of oxonium salts for these compounds; for example,—

$$C_6H_5\cdot NH\cdot N:C_6H_4:O(H \text{ or } C_2H_5)Cl.$$

The formulation of the salts of the ethers and parent substances is thus the same, whilst the reactions in concentrated sulphuric acid solution are easily explained.

DISCUSSION.

Mr. TUCK said that the absorption spectra of the hydrochlorides of the free *p*-hydroxyazo-compounds and their ethers were the same, and this fact showed that their constitutions therefore were identical. If this was so, then

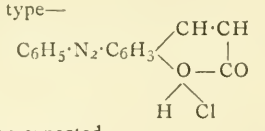
Dr. Hewitt's conclusion (*Ber.*, 1897, xxx., 1625), that hydrochloric acid converted the *p*-hydroxyazo-compounds into quinonehydrazones, must be incorrect. This was now accepted by Dr. Hewitt.

As the absorption spectra of these hydrochlorides agreed with that of azobenzene hydrochloride, one must conclude that the acid was combined in precisely the same manner in each case; that is, the hydrochlorides were true azo-derivatives.

The objection to Dr. Hewitt's formula for the hydrochlorides lay in the fact that it was impossible to assign the same structure to azo-benzene hydrochloride as he did to hydroxyazo-hydrochlorides.

Mr. Baly pointed out that Dr. Hewitt's explanation seemed to fail in two respects. In the first place, it could not account for the formation of the deeply coloured hydrochloride of azobenzene where, of course, the oxonium structure was excluded. Moreover, the change of colour on adding hydrochloric acid to a neutral solution of azobenzene was precisely of the same character as Dr. Hewitt had shown in the case of the hydroxyazo-compounds. In the second place, the addition of the acid molecule to the oxygen atom with the formation of the oxonium salt would undoubtedly decrease the colour of the compound in the sense that the absorption band would shift towards the *blue*. In the hydrochlorides of the hydroxyazo-compounds, the absorption band had shifted towards the *red*, causing the salt to be bluer than the parent substance. This decrease in colour would be caused by the decrease in the residual affinity of the system, due to the oxygen becoming quadrivalent.

Mr. H. V. Mitchell drew attention to the fact that he had been unable to prepare a hydrochloride of benzeneazocoumarin (*Trans.*, 1905, lxxxvii., 1231), whereas if the view put forward by the authors were correct, a hydrochloride of the type—



might have been expected.

Dr. Hewitt, in reply, pointed out that Mr. Tuck stated definitely in his paper, "the hydrochlorides of the free hydroxyl substances have an azo-structure," whilst Mr. Baly's arguments derived from the properties of benzeneazo-*p*-cresol and its derivatives depended for their validity on this substance being a quinonehydrazone. Since this point was still disputed and the bulk of the evidence seemed to be in favour of a hydroxylic structure for the free *o*-azo-compounds, the arguments lost in weight.

No surprise need be occasioned by Mr. Mitchell's inability to obtain a hydrochloride from benzeneazocoumarin, for the lactonic oxygen atom would scarcely have pronounced basic properties, whilst Professor Armstrong's arguments against the formula depended on supposed basicity of the benzene nucleus and non-existence of oxonium salts. Basicity of the benzene nucleus scarcely accorded with the feeble acidity of phenol and the diminishing basicity observed in amines by introduction of benzene nuclei, whilst the possibility of oxonium salt formation was recognised by all who had made a comparative study of the xanthhydrol and acridinium groups.

*2. "*A New Method of Determining Vapour Densities.*" (Part I.). By Philip Blackman.

*3. "*Studies in the Camphane Series.* Part XXV. *Action of Diazomethane on the Two Modifications of* iso-*Nitrosocamphor.*" By Martin Onslow Forster and Henry Holmes.

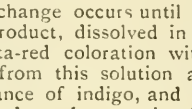
When diazomethane acts on the stable *iso*nitrosocamphor (m. p. 152°) dissolved in ether the N-methyl ether is produced, whilst the unstable modification (m. p. 114°), treated with a deficit from one molecular proportion of the agent, merely undergoes isomeric change to the less fusible variety; in view of this observation, some caution will be necessary in drawing conclusions regarding the structure of a compound based on its behaviour towards diazomethane. The benzaldoximes do not behave in the same way, benz*anti*-aldoxime (m. p. 35°) yielding the O-methyl ether, whilst the *syn*-aldoxime (m. p. 128°) remains unchanged.

By the action of *p*-nitrobenzyl chloride on an alcoholic solution of *iso*nitrosocamphor in presence of sodium ethoxide, three products arise. The *compound*, $C_{17}H_{20}O_4N_2$, having the composition of a nitrobenzyl ether of *iso*nitrosocamphor, crystallising in pale brown prisms, melting at 175°, and having $[\alpha]_D$ 123·0°; the *compound*, $C_{17}H_{18}O_3N_2$, forming lustrous, transparent, yellow plates, melting at 214°, with $[\alpha]_D$ −65·3°, and an *oil*, which is characterised by developing an intense blue coloration when caustic alkali is added to a solution in methyl, ethyl, or *iso*butyl alcohol. If silver oxide is substituted for sodium ethoxide as a condensing agent, and *p*-nitrobenzyl chloride is replaced by the bromide, an isomeric *compound*, $C_{17}H_{20}O_4N_2$, is produced, crystallising in colourless prisms, melting at 114°, and having $[\alpha]_D$ 138·0°.

On mixing an ethereal solution of iminocamphor with formaldehyde, no change occurs until a trace of acid is added, when the product, dissolved in alcohol, develops an intense magenta-red coloration with caustic alkali; ether precipitates from this solution an unstable solid, having the appearance of indigo, and yielding camphorquinone, formaldehyde, and ammonia with dilute sulphuric acid.

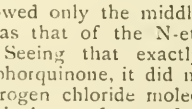
Camphorquinone is rapidly oxidised by an aqueous solution of hydrogen peroxide to camphoric anhydride.

The N-*ethyl* ether of *iso*nitrosocamphor,—



produced in association with the O-ethyl ether when ethyl iodide acts on *iso*nitrosocamphor in presence of sodium ethoxide, melts at 57°, and has $[\alpha]_D$ 248·1°; it is readily hydrolysed by acids, yielding camphorquinone and ethylhydroxylamine.

Discussion.

Mr. Baly said that the formulæ for the two forms of *iso*nitrosocamphor which Dr. Forster referred to as being given by Baly, Marsden, and Stewart had resulted from the adverse criticism their paper received when it was read. When their paper was first written, they had inclined to the nitroso-formula, and it was therefore extremely interesting to find that Dr. Forster's experiments seemed to support this view. As regards the new formula which Dr. Forster had given to the N-ethers of *iso*nitrosocamphor, he (Mr. Baly) spoke strongly in favour of it from the point of view of the absorption spectra of these substances. They exhibited a very marked absorption band, exactly the same as that which might be described as the middle band of *p*-benzoquinone. The latter substance in aqueous solution exhibited three absorption bands, the middle one of which was absent from the spectrum of an alcoholic solution. It had occurred to him that the middle band might be explained by the formation of a hydrate of quinone, and so the absorption spectrum was examined of an alcoholic solution of *p*-benzoquinone to which a little alcoholic solution of hydrogen chloride had been added. The absorption spectrum then showed only the middle band, and was, indeed, the same as that of the N-ethyl ethers of *iso*nitrosocamphor. Seeing that exactly the same was observed with camphorquinone, it did not seem unreasonable that the hydrogen chloride molecule combined by virtue of the quadrivalency of one of the oxygen atoms, and that in the case of camphorquinone a compound was formed of the type  . The analogy between this and Dr. Forster's new formula was sufficient to account for the similarity in the spectra of camphorquinone dissolved in alcohol containing some hydrogen chloride

and the N-alkyl ethers of *iso*nitrosocamphor. There was no doubt that the absorption spectra offered striking evidence against either of the varieties of *iso*nitrosocamphor having the formula $C_8H_{14}\begin{cases}C{:}NH{:}O\\ |\\ C{:}O\end{cases}$, for there was no resemblance between the spectra of the *iso*nitroso-compounds and the N-alkyl ethers.

Dr. Hewitt asked Mr. Baly if he had convinced himself that the colourless additive product of benzoquinone and hydrochloric acid was not really chloroquinol.

4. "*The Oxidation of Aromatic Hydrazines by Metallic Oxides, Permanganates, and Chromates.*" By Frederick Daniel Chattaway.

Primary aromatic hydrazines are readily attacked by most substances capable of giving up oxygen at all easily. The products are in the main the same as those which are formed by free oxygen.

The chief action, which results in the replacement of the hydrazino-group by hydrogen and the liberation of nitrogen, is generally accompanied by secondary ones which take place to a relatively very small extent. By these secondary actions, hydrocarbons of the diphenyl group or azo-derivatives are formed. Diazo-compounds are only obtained in presence of acids; in presence of alkalis, they are not formed.

Potassium chromate oxidises primary aromatic hydrazines very easily, and gives a theoretical yield of nitrogen and hydrocarbon. This reaction affords the most convenient method yet described for replacing an aromatic amino-group by hydrogen, the diazonium group yielded by it being first reduced to the hydrazino-group, and this then replaced by hydrogen through oxidation with potassium chromate.

All the evidence obtained shows that the explanation of the behaviour of primary aromatic hydrazines on oxidation recently put forward by the author is correct (*Trans.*, 1907, xci., 1324), namely, that an unstable hydroxy-hydrazine is first produced, which, in presence of caustic alkali, immediately breaks down into hydrocarbon, nitrogen, and water:—

$$\begin{matrix}R{\cdot}N{\cdot}H\\ |\\ H{\cdot}N{\cdot}OH\end{matrix} \Rightarrow \begin{matrix}R\\ |\\ H\end{matrix} + \begin{matrix}N\\ \|\\ N\end{matrix} + \begin{matrix}H\\ |\\ OH\end{matrix}.$$

Copper oxide easily gives up its oxygen to phenylhydrazine, and if the reduction is conducted under suitable conditions the metal can be deposited on glass in the form of a fine mirror. The film of metal thus laid down is as brilliant as a similar deposit of silver, and shows the beautiful red colour of polished copper.

5. "*Studies in Fermentation.* Part II. *The Mechanism of Alcoholic Fermentation.*" By Arthur Slator.

The velocity of the conversion of dextrose, lævulose, galactose, and mannose into alcohol and carbon dioxide by the action of living yeast has been measured in the manner already described (*Trans.*, 1906, lxxxix., 128). The main results are as follows:—

1. The rate of fermentation of dextrose, lævulose, galactose, and mannose is approximately independent of the concentration of the sugar between the concentrations 1 grm. to 10 grms. per 100 cc.

2. The fermentation of dextrose and lævulose under all conditions proceeds with approximately equal velocities.

3. The temperature-coefficient is almost the same in the case of the fermentation of dextrose, lævulose, and mannose, but is somewhat less in the case of the fermentation of galactose.

4. Many yeasts (very probably all yeasts) are unable to ferment galactose unless the yeast has been grown in the presence of this sugar.

5. The ratio of the rate of fermentation of dextrose to mannose varies greatly, depending on the treatment the yeast has undergone.

6. When two sugars are fermented simultaneously in the same solution, interference takes place between the reactions.

7. The velocity of fermentation by living yeast can be easily lessened by the addition of certain inhibiting agents, but cannot be appreciably raised.

8. In all probability the fermentation of sugars by preparation from yeast proceeds on the same lines as that by living yeast, but the reaction is much complicated by secondary changes.

The supposition that the reaction which has the main control of the velocity of fermentation is the decomposition of a stable compound between the enzyme and the sugar can be made to explain these results. Possibly three enzymes are present in yeast which will ferment the four sugars:—Glucozymase which ferments dextrose and lævulose, galactozymase which ferments galactose, and mannozymase which ferments mannose.

6. "*Organic Derivatives of Silicon.* Part IV. *The Sulphonation of Benzylethylpropylsilicyl Oxide and of Benzylethyldipropylsilicane.*" By Herbert Marsden and Frederic Stanley Kipping.

Although the optically-active silicon compounds described recently (Kipping, *Trans.*, 1907, xci., 212) were actually prepared from the product of the sulphonation of benzylethylpropylsilicol, their investigation indicated that they were sulphonic derivatives of benzylethylpropylsilicyl oxide. As this view of their constitution seemed to need some confirmation, the authors have prepared benzylethylpropylsilicyl oxide itself and sulphonated it with sulphuric and with chlorosulphonic acid; in both cases there was formed an acid having the composition of a derivative of the oxide, and identical with the compound which has been resolved; any uncertainty regarding the composition of the optically-active compounds is thus removed.

The sulphonation of phenylbenzylethylpropylsilicane with chlorosulphonic acid gave results similar to those obtained with sulphuric acid; that is to say, the phenyl group was eliminated and the product was a sulphonic derivative of benzylethylpropylsilicyl oxide identical with that previously described.

Benzylethyldipropylsilicane, $BzEtPr_2Si$, has been prepared and converted into *benzylethyldipropylsilicanesulphonic acid*, $EtPr_2Si{\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3H$, with the aid of chlorosulphonic acid; the *l-menthylamine*, *cinchonidine*, and *quinine* salts of this acid resemble very closely the corresponding salts of *dl*-benzylmethylethylpropylsilicanesulphonic acid (*loc. cit.*, p. 717), a fact which indicates that the latter are mere mixtures of their optically-isomeric components.

Diphenylethylsilicyl chloride, $Ph_2EtSiCl$, a colourless liquid boiling at 206—208° (50 mm.), *diphenylethylsilicyl oxide*, $(Ph_2EtSi)_2O$ (m. p. 65·5.), *triphenylethylsilicane*, Ph_3EtSi (m. p. 76°), and *triphenylmethylsilicane*, Ph_3MeSi (m. p. 67—67·5°) were also described.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, January 24th, 1908.

Prof. J. Peery, F.R.S., President, in the Chair.

Mr. R. S. Smith and Mr. J. G. Howarth were elected Fellows of the Society. Mr. W. C. Campling was elected a Student member of the Society.

A paper by Mr. W. Rosenhain on "*Observations on Recalescence Curves*" was read by Dr. R. T. Glazebrook.

Referring to the importance of the accurate study of recalescence phenomena in metals and alloys, the author describes the two principal methods employed for obtaining recalescence curves. These are known as the "Inverse Rate" and "Differential" methods respectively. In the former method the time occupied by successive equal decrements of temperature are observed and plotted against the temperature of the cooling body, thus giving a

curve whose ordinates are temperature (t) and dT/dt (T = time) respectively. In the differential method the difference of temperature between the body under observation and a neutral or "blank" body cooling under approximately the same conditions is observed and plotted against the temperature of the body. The physical interpretation, in terms of quantity of heat evolved and of rate of evolution of heat of these two kinds of curves, are discussed by reference to the fundamental curve representing the time-temperature relations of one or two cooling bodies. On both types of curve, recalescences are indicated by peaks, and it is shown that in the case of an inverse-rate curve the area of a peak when taken between proper limits is roughly proportional to the quantity of heat evolved divided by the rate of cooling. Serious errors affecting this proportionality in practical cases are, however, pointed out. The differential curves are first discussed for the ideal case in which the neutral body cools at the same average rate as the body under observation, but it is pointed out that this case cannot be readily attained in practice. The effect of differences in the rates of cooling of the two bodies is shown to be the production of a general slope in the differential curve, upon which peaks due to recalescences are superposed. The author suggests the elimination of this general slope by plotting a "derived differential curve" in which the movements of the differential galvanometer during the process of cooling through successive intervals of temperature are plotted against the temperature of the cooling body. This curve represents the differential coefficient of the ordinary differential curve. Peaks representing recalescences on these curves are shown to have exactly the same physical meaning as peaks on the inverse-rate curves, and the conclusion is arrived at that the two methods lead to identical results, the choice between them being thus reduced to a question of experimental expediency. The experimental requirements of the two methods are then described, and it is shown that to arrive at the same degree of accuracy in the curves, the means of measuring temperature used for the inverse-rate method must be very much more sensitive than those required for the differential method. This necessity arises from the fact that in the inverse-rate method the actual temperature of the cooling body must be determined to the same degree of accuracy as the difference of temperature between the two bodies in the differential method, and while the latter difference rarely exceeds 40° C., the former frequently attains 800° C. The fact that accurate autographic methods appear to be more readily attainable with the differential method is also an argument in its favour, as is also the fact that it is less subject to accidental error from external disturbing causes.

The theoretical views advanced in this discussion are then illustrated by a series of actual recalescence curves, chiefly of steel, taken by both methods. These illustrate the advantages of plotting the results in the form of the derived differential curves. This is particularly apparent in the case of three recalescence curves taken of samples of the same steel, in which the rate of cooling was varied from one and three-quarter hours to twelve minutes. With the more rapid cooling, the ordinary differential curves become very oblique and unintelligible, but the derived differential curves are quite definite in character and are in good agreement with one another. The author, however, advocates the determination of recalescence curves by observations on gradual cooling rather than on the rapid cooling sometimes adopted. A recalescence curve obtained by a modification of the differential method in which the cooling of two pieces of the same steel is utilised, is also shown; in this curve a recalescence is indicated by a forward swing of the galvanometer followed by an equal and opposite swing.

Finally, the author describes a recalescence first observed to occur somewhat mysteriously in the body of certain furnaces at a temperature of 580° C. This was ultimately traced to a transformation occurring in crystalline silica, whether free or in admixture with porcelain or fire-clay. Heating- and cooling curves of quartz-sand are given, showing this recalescence vigorously. The author points out that this recalescence in crystalline silica coincides with certain points in the iron-carbon diagram of Roberts-Austen and of Carpenter and Keeling, and suggests that the recalescences observed by those workers may have arisen from silica in their furnaces.

Mr. F. J. SELBY remarked on the skill with which the author, by direct reasoning from certain approximate assumptions, had arrived at his interesting results as to the points of importance in connection with recalescence curves. Mr. Rosenhain had shown, very clearly and graphically, that from the theoretical point of view all the methods of representing the cooling-curves must give identical information, and that therefore the decision as to method to be adopted depended simply on the experimental accuracy attainable; while, in this respect, he had brought forward very strong evidence in favour of the Roberts-Austen differential method. Mr. Selby suggested that it might be worth while to draw out theoretical cooling-curves based on certain simple assumptions as to the conditions of cooling. He showed how this might be done for the parts of the curve preceding and following the recalescence; and that by making a suitable supposition as to the variation in the rate of evolution of heat during the recalescence, such as $dQ/dT = (a - bT)^2 e^{cT}$, a complete theoretical curve might be drawn by the comparison of which with the experimental curve the constants might be determined, and all the quantities of importance in connection with the recalescence estimated with greater accuracy. In particular, and without any assumption as to the form of dQ/dT, some of the results in the paper could be verified; it could be shown that the evolution of heat was not completed at the peak on the derived differential curve (the point of inflection on the Roberts-Austen curve), and the point of maximum evolution of heat on the experimental curve could be fixed. The value of the derived differential curve advocated by the author becomes apparent from such calculations.

Mr. A. CAMPBELL remarked that the end of the paper was the part which would most likely be of interest to physicists. It was most interesting to find that the author has shown (by the cooling-curve method) a change-point in silica near 580° C. Quite a number of years ago Le Chatelier showed that between 460° and 500° C. the coefficient of expansion of quartz showed a quick increase, and he predicted that a change-point should occur at 270° C. Randall's experiments in 1905 on quartz showed a similar result so far as the expansion is concerned. Experiments which he (Mr. Campbell) had made with nickel showed no abnormality in coefficient of expansion at temperatures which gave strongly marked thermo-electric change-points. For the direct reading of rates of cooling, Dejean not long ago devised an ingenious arrangement in which the thermocouple is connected to one coil of a differential moving-coil galvanometer whose other coil is connected to a second galvanometer: the readings of the latter will be a function of the rate of cooling. It occurred to the speaker that a transformer would give a simpler method of obtaining di/dt, but the slowness of change of i makes it too insensitive. The assumptions made in the paper that the specific heat, the thermal conductivity, and the emissivity of any material remain approximately constant even over a small range of temperature near recalescence, seem somewhat uncertain to the physicist, and must be regarded merely as working conventions by the metallurgist.

Mr. S. W. J. SMITH expressed his interest, from the consideration of magnetic data, in the author's opinion that there is no critical point near 580° C. in the cooling-curves of iron and steel. It was curious that in the paper in which Roberts-Austen describes the critical point found at about 580° C., he cites the magnetic experiments of Morris in support of the fact that a change occurs in iron at that temperature. Morris puts the temperature of the magnetic change at about 550° in one specimen, but at

about 500° in another; while in a third the effect was scarcely observable. Even in the specimen most studied, the magnitude of the effect seemed to depend upon the annealing temperature. In some experiments on permeability-temperature variation in nearly pure iron (0·06 per cent C., 0·1 per cent Mn) annealed at about 850° C., Mr. Satterly and the speaker found a distinct change in the slope of the $\mu-\theta$ curve (H=0·43) slightly below 500° during cooling, and a distinct minimum value of μ near 250° during heating. But with the field-strength used there was no apparent break in the slope of the $\mu-\theta$ curve near 580° C. There was thus apparently no conclusive evidence from magnetic data of a critical point at 580° C. The effect observed at 580° by Roberts-Austen was very feeble compared with another effect which began near 500° and continued over a considerable range. This effect was obvious as a more or less pronounced "hump," of which the maximum lies near 400° on practically all the permeability-curves. It was even traceable in the curves of Hopkinson, although his observations below 500° were very few in number. Their own magnetic experiments agreed with those of Morris and with the Roberts-Austen cooling curve in showing another critical point near 250°, although in their case the effect was only detected during heating.

A paper by Mr. W. C. M. Lewis entitled "*An Experimental Examination of Gibbs' Theory of Surface Concentration regarded as the Basis of Adsorption, and an Application to the Theory of Dyeing*" was postponed.

ROYAL INSTITUTION.

General Monthly Meeting, February 3rd, 1908.

Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair.

Lord Ellenborough and Mr. Alfred Moseley, C.M.G., were elected Members. The Honorary Secretary reported the decease of the Right Hon. Lord Kelvin, O.M, G.C.V.O., P.C., D.C.L., LLD., D.Sc., F.R.S., Grand Officer of the Legion of Honour, Chancellor of the University of Glasgow, on the 17th of December, 1907, and the following Resolution was passed.

> *Resolved*, That the Managers of the Royal Institution of Great Britain desire to record at this, their first meeting subsequent to his death, their sense of the great loss sustained by the Institution and by Science in the decease of Lord Kelvin.

Lord Kelvin became a Member of the Royal Institution in 1886. He gave his first lecture at the Royal Institution at the time when Faraday was engaged in his epoch-making researches on Electricity and Magnetism; and between the years 1856 and 1900 Lord Kelvin delivered a Course of Lectures on The Electric Telegraph in 1863, and no less than nine Friday Evening Discourses on the following subjects:—"The Origin and Transformations of Motive Power" (1856), "Atmospheric Electricity" (1860), "Tides" (1875), "Effects of Stress on Magnetisation of Iron, Nickel, and Cobalt" (1878), "The Sorting Demon of Maxwell" (1879), "Elasticity viewed as possibly a Mode of Motion" (1881), "Isoperimetrical Problems" (1893), "Contact Electricity of Metals" (1897), "Nineteenth Century Clouds over the Dynamical Theory of Heat and Light" (1900).

On the occasion of the celebration of the Jubilee of his appointment to the Chair of Natural Philosophy in the University of Glasgow, an address of congratulation was presented to Lord Kelvin on behalf of the Members of the Royal Institution, expressing their high appreciation of the conspicuous services rendered by him in the extension and diffusion of scientific knowledge.

When Lord Kelvin resigned his Professorship and came to reside in London he took much interest in the Royal Institution, and became a Manager in 1892.

The Managers desire to offer on behalf of the Members of the Royal Institution the expression of the most sincere sympathy with Lady Kelvin and the family in their bereavement.

The Special Thanks of the Members were returned to Dr. W. J. Russell, F.R.S., for his donation of £100 to the General Fund; and to Mr. Charles Hawksley for his donation of £100 (in commemoration of the 100th anniversary of the birth, on July 12th, 1807, of Thomas Hawksley, F.R.S., Civil Engineer), to the Fund for the Promotion of Experimental Research at Low Temperatures.

Letters were read from Prof. A. Haller, Prof. L. Troost, and Prof. W. Spring acknowledging their election as Honorary Members of the Royal Institution.

The Chairman announced that the Managers had appointed Dr. Kenneth Robert Hay, M.B. (Cambridge), Medical Officer to the Royal Institution in succession to the late Dr. Woodhouse Braine, who held the appointment for thirty-six years.

NOTICES OF BOOKS.

A Text-book of Organic Chemistry. By A. F. Holleman, Ph.D., F.R.A.Amst. Translated by A. Jamieson Walker, Ph.D. (Heidelberg), A.A., assisted by Owen E. Mott, Ph. D. (Heidelberg). Second English Edition. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1907.

The original Dutch edition of this work proved a valuable and in some respects unique text-book of organic chemistry for the beginner, and the translations into English, German, Italian, and Russian have been equally well received. The great advantage of its use to the student is the special prominence given to theory, and in particular to the structure of the compounds considered. The empirical facts enumerated are reduced to the minimum which is compatible with a thorough elementary knowledge of organic chemistry, while the attention of the student is concentrated upon general reactions and principles. The book is well up to date, and gives full accounts of the application of physico-chemical methods to organic substances, and brief notes are added upon some important technical processes. In the second English edition the text has been completely re-written, Prof. Holleman himself having given the translators valuable assistance in the selection and arrangement of the new material.

Traité Complet d'Analyse Chimique Appliquée aux Essais Industriels. ("Complete Treatise of Technical Chemical Analysis.") By J. Post and B. Neumann. Second French Edition, edited by Dr. L. Gautier. Vol. II., Part I. Paris: H. Hermann. 1908.

Part I. of Volume II. of this comprehensive treatise deals with chalk, mortar and cements, the ceramic industry, and glass making. The choice of analytical methods is above criticism, and in every respect it is clear that thoroughness has been the special aim of the compilers. The translator, Dr. L. Gautier, has made many additions to the text, and has taken every care to make the French edition as valuable and trustworthy as the German.

Royal Institution.—On Tuesday next, February 11, at 3 o'clock Prof. Stirling begins a course of six lectures at the Royal Institution on "Membranes—Their Structure, Uses, and Products"; and on Saturday, February 15, at the same hour, Mr. Selwyn Brinton commences a course of three lectures on "The Art of Florence." The Friday Evening Discourse on February 14 will be delivered by Dr. C. W. Saleeby on "Biology and History," and on February 21 by Sir Oliver Lodge on "The Ether of Space."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 1, January 6, 1908.

New Homologues of Diglycollic Acid.—E. Jungfleisch and M. Godchot.—α-Ethyl α_1-methyl diglycollic acid on distillation *in vacuo* at 140—150° gives up water and is partially transformed into anhydride. It is completely dehydrated by the action of boiling acetyl chloride, and on distillation α-ethyl α_1-methyl diglycollic anhydride,—

$$\begin{array}{c} {\scriptstyle(\alpha)} \\ CH_3—CH_2—CH—CO \\ \qquad O< \qquad >O, \\ CH_3—CH—CO \\ {\scriptstyle(\alpha_1)} \end{array}$$

is isolated. The diethyl derivative of α-ethyl α_1-methyl diglycollic acid yields the corresponding diamide with alcoholic ammonia,—

$$NH_2—CO—CH(CH_2—CH_3)—O—CH(CH_3)—CO—NH_2.$$

$\alpha\alpha$-Dimethyl α_1-methyl diglycollic acid,—

$$\begin{array}{c} COOH—C(CH_3)_2—O—CH(CH_3)—CCOH, \\ {\scriptstyle(\alpha)} \qquad\qquad {\scriptstyle(\alpha_1)} \end{array}$$

is prepared by the action of ethyl α-bromoisobutyrate on sodium ethyl lactate. The diethyl ether of α-isopropyl α_1-methyl diglycollic acid,—

$$\begin{array}{c} COOH—CH[CH=(CH_3)_2]—O—CH(CH_3)—COOH, \\ {\scriptstyle(\alpha)} \qquad\qquad {\scriptstyle(\alpha_1)} \end{array}$$

is formed when ethyl bromo-isovalerianate is substituted for ethyl bromo-isobutyrate in the above reaction.

Mechanism of Phenyl Transpositions in Iodohydrines and Aromatic Glycols.—Marc Tiffeneau.—The author has shown that the α-glycols, α-chlorhydrines, and tetra-substituted oxides of ethylene, poly-substituted aromatic glycols of general formulæ $Ar—CHOH—COH<\begin{matrix}R\\R'\end{matrix}$ and $Ar—CHOH—CHOH—Ar'$, and aromatic halogen hydrines of general formulæ $Ar(R)=C(OH)—CHX—R'$ and $Ar—CHOH—CX=RR'$, are capable of undergoing molecular transpositions when converted into aldehydes or ketones. Thus certain reagents convert the halogen hydrines, $Ar—CHOH—CHX—R$, into ethylene oxides without any transposition,—

$$Ar—CHOH—CHX—CH_2 \xrightarrow{-HX} Ar—CH\begin{matrix}—CH—CH_3,\\ \diagdown O \diagup\end{matrix}$$

while others act as follows:—

$$Ar—CHOH—CHX—CH_3 \xrightarrow{-HX} Ar—CH<\begin{matrix}CHO\\CH_3\end{matrix}.$$

The same differences are observed with the corresponding ether oxides, $Ar—CH(OR)—CHX—R$. The author has shown that a mono-ether, such as $C_6H_5—CH(OCH_3)—C(OH)(CH_3)_2$, does not undergo the following change, giving a methoxystyrolene compound,—

$$C_6H_5—CH(OCH_3)—C(OH)(CH_3)_2 \xrightarrow{-H_2O} C_6H_5—C(OCH_3)=C(CH_3)_2,$$

but yields dimethylphenylacetaldehyde,—

$$C_6H_5—CH(OCH_3)—C(OH)(CH_3)_2 \xrightarrow{-CH_3OH} CHO—C<\begin{matrix}C_6H_5\\(CH_3)_2\end{matrix}$$

MISCELLANEOUS.

South-Western Polytechnic, Chelsea.—The Lord Alverstone, G.C.M.G., Lord Chief Justice of England, presents Prizes and Certificates to Students of Evening Classes and Day College on March 13 at 8 o'clock p.m.

Acid Properties of Ozone.—W. Manchot and W. Kampschulte.—With ammonia at the ordinary temperature ozone forms dense mists, which do not contain nitric oxide. Similar phenomena are observed with organic bases such as methylamine, trimethylamine, piperidine, &c., and with strong bases it is more marked than with weak. Ozone forms compounds with the caustic alkalis, and the stability of the compound decreases as the atomic weight of the metal falls; thus the cæsium derivative is the most stable, and the lithium derivative the least. Mg, Ca, Sr, and Ba oxides destroy ozone rapidly at the temperature of the room, and heat is evolved by the reaction. The compounds formed are decomposed by water. The acid properties of ozone are also shown by the fact that blue litmus is coloured distinctly red, and other indicators give a decidedly acid reaction with it. It makes water conduct an electric current. The acid properties of ozone seem to belong partly to a decomposition product which appears to be the decomposition product of a hydrate of ozone. The mist formed with ammonia must contain this product.—*Berichte*, xl., No. 18.

Institute of Chemistry.—*January Examinations*, 1908.—Of twenty-three candidates who presented themselves for the Intermediate Examination, the following fourteen passed:—W. Cameron; F. Challenger, B.Sc. (Lond.); P. W. Copeland, B.Sc. (Lond.); G. A. M. Cunningham; H. Davies; J. G. Hay; A. Hepburn; H. R. Jensen, B.Sc. (Liverpool); C. H. Kirkaldy; F. W. Linch; W. A. Riley; V. J. Tilley; R. Unwin; and C. H. Warner. In the Final Examination for the Associateship, of four candidates who presented themselves in the branch of Mineral Chemistry, the following three passed:—S. L. Archbutt; C. P. Matthews, B.Sc. (Lond.); and L. A. Levy, B.A. (Cantab.), B.Sc. (Lond.). One candidate presented himself in Physical Chemistry, and passed:—N. P. Campbell, B.A. (Oxon.). Of six in Organic Chemistry, three passed:—T. P. Hilditch, B.Sc. (Lond.); B. D. Porritt, B.Sc. (Lond.); and H. E. Watson, B.Sc. (Lond.). Eight candidates presented themselves in the Chemistry of Food and Drugs, of whom the following seven passed:—A. P. Davson, Assoc.R.C.Sc. (Lond.); A. G. Harrington; H. Mansfield, B.Sc. (Lond.); R. D. Masson; P. Murphy; B. F. Sawbridge, B.A. (Oxon.); and J. M. Wilkie, B.Sc. (Lond.). W. P. Hayworth, A.I.C., also passed this examination in order to obtain the special certificate recognised by the Local Government Boards. Four candidates presented themselves for examination for the Fellowship, and the following three passed:—W. Barbour, M.A., B.Sc. (St. Andrews), in the Branch of Organic Chemistry; P. V. Dupré, A.C.G.I., in Mineral Chemistry; and A. C. Franklin, in Metallurgical Chemistry.

MEETINGS FOR THE WEEK.

MONDAY, 10th.—Society of Arts, 8. (Cantor Lecture). "Theory and Practice of Clock Making," by H. H. Cunynghame, C.B.

TUESDAY, 11th.—Royal Institution, 3. "Membranes—Their Structure, Uses, and Products," by Prof. William Stirling, M.A., LL.D., D.Sc., &c.

WEDNESDAY, 12th.—Society of Arts, 8. "The Application of Science to Foundry Work," by R. Buchanan.

THURSDAY, 13th.—Society of Arts, 4.30. "The New Imperial Gazetteer of India," by Richard Burn, I.C.S.

—— Royal Institution, 3. "The Story of the Spanish Armada," by Major Martin Hume.

FRIDAY, 14th.—Royal Institution, 9. "Biology and History," by Dr. C. W. Saleeby.

—— Physical, 8. Annual General Meeting. President's Address.

SATURDAY, 15th.—Royal Institution, 3. "The Art of Florence," by Selwyn Brinton, M.A.

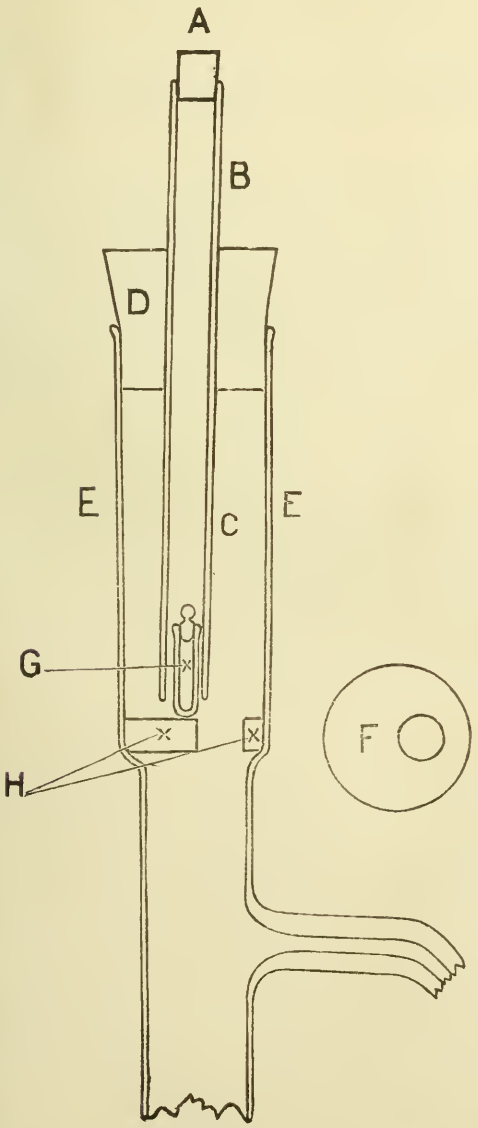
THE CHEMICAL NEWS.

Vol. XCVII., No. 2516.

A SIMPLE FORM OF RELEASE FOR VICTOR MEYER'S VAPOUR-DENSITY APPARATUS.

By T. S. PATTERSON.

The following simple release may be found convenient for fitting to the ordinary type of Victor Meyer's vapour-density apparatus, and it may be found to present advantages over other forms of release presently in use.



The figure shows the upper part of the neck of an ordinary Victor Meyer apparatus. A narrow slice, F —about a quarter of an inch in thickness—is cut from a cork which just fits into the wide part, E, of the neck, and excentrically in this slice is bored a small hole a quarter of an inch in diameter. The slice of cork is then placed fairly firmly in position, as shown (in section) at H. The open end of E is fitted with a rubber stopper, D, through which a hole is bored *in a slanting direction* to take the glass tube, B C, of about a quarter inch bore. This tube is closed by the small rubber stopper A. (The apparatus should be so arranged that a line drawn lengthwise through the centre would stand vertical).

When, in the course of a determination, the bulb of the apparatus has been heated so long that no further expulsion of air takes place, the stopper, A, is removed, and the little Hofmann tube, G, containing a weighed quantity of the substance to be investigated is dropped into the position shown in the figure, after which the stopper, A, is firmly replaced. In order to drop the Hofmann tube into the bulb at the desired time, the tube, B C, is moved by hand (the elasticity of the rubber stopper D permitting of this without any leak), so as to bring its lower end just over the hole in the cork, H, when the tube, G, drops into the bulb of the apparatus.

An advantage of this arrangement is that the little tube is kept always in a vertical position and no leakage can occur until the hot region of the bulb is reached.

Organic Chemistry Laboratory,
Glasgow University.

NOTE ON THE CUTTING OF SODIUM.

By D. P. McDONALD, M.A.

In cutting sodium by means of the Gattermann knife considerable difficulty constantly arises from the fact that the metal, becoming slightly warmed by the hand and by the friction of cutting it, softens, and is very apt to stick to the blade of the knife.

This difficulty may readily be overcome if, from time to time when signs of softening occur, the lump of sodium is dipped in anhydrous ether for a moment or two. The metal is chilled by the immersion, and further cooled by the evaporation of the liquid left on the surface after removal from the ether, and can then be cut with great ease. The cut slices are generally dropped into a basin containing ether, and the same ether of course serves for cooling the stick which is being cut.

Organic Chemistry Laboratory,
Glasgow University.

MODE OF VALUING RAW RUBBER.

By CLAYTON BEADLE and HENRY P. STEVENS.

In a previous paper entitled "The So-called 'Nerve' of Rubber" (Chemical News, 1907, xcvi., 247) we have given details of mechanical tests on raw rubbers both before and after mechanical treatment and exposure to low temperatures. The results of these tests show clearly that the tensile strength and resiliency of a rubber are enormously influenced by the conditions to which the test piece is subjected. We do not claim to have brought forward anything especially novel in this communication, as the principle which we have sought to demonstrate has long been recognised by manufacturers.

In spite, however, of all this, we find in recent published researches on the subject a general tendency to overestimate the importance to be attached to the properties of raw rubbers, and to pay little or no attention to the properties of the vulcanised product.

We find tables of figures giving the tensile strength and other physical properties of raw rubbers, without any explanation of the methods employed in getting the test

pieces in suitable form for applying the tests or of the temperature to which the samples have been exposed.

To consider only the latter point. In the paper above referred to, we gave results obtained with the same rubbers before and after exposure to a low temperature; a sample of masticated rubber may have its tensile strength increased several fold by freezing or even cooling at a winter's temperature. It is therefore obvious that a sample tested after it has lain a few days in a cold room in winter will give a higher tensile strength than a sample which in summer would not have been exposed to these conditions.

If, then, figures for the physical properties are to be of value and capable of comparison with one another, the rubbers must all be treated under carefully specified conditions, probably from the time of coagulation onwards. But it must readily be seen that such a procedure is entirely out of the question.

In attempting to ensure such normal treatment, it would probably be best to take as a guide the process employed in the manufacture of cut sheet. The dry rubber should first be masticated between rolls at a uniform speed, at a fixed distance apart and for a definite length of time. To get uniform results rolls of the same dimensions should always be used, and the same quantity of rubber taken for mastication. The temperature would have to be maintained at a constant figure for all samples, and a given number of foot-pounds of work would have to be applied to each sample. When the mastication is finished, the rubber should be rolled to a uniform sheet of, say, 1 mm. in thickness for cutting test pieces. The sample may then be tested straight away, a portion being set aside and cooled to 0° C. in an ice-chest for a definite period—say, one week—and again tested.

This is a rough outline of what may be suggested as a possibly reliable method for obtaining uniform results.

Even then the results may not be found to be of any very extraordinary value, but a number of tests on these lines would be of great interest, and if the rubbers were also vulcanised under uniform conditions and tested, it would be of great interest to note in how far there exists a correlation in properties between the raw and vulcanised rubbers.

To correlate the properties of rubbers before and after vulcanisation would involve an immense amount of research, and at the end of it all it is highly doubtful whether there exists any relationship of a useful order. On the other hand, random tests carried out on crude rubbers under conditions anything but uniform can be of no practical value, but must inevitably mislead.

Such a procedure is, however, far more laborious and complex than performing on each sample, as we do, a series of vulcanisations until the right conditions of vulcanisation are discovered, and then comparing the results so obtained by physical tests with similar tests performed on some well-known brand after proper vulcanisation, such, for instance as hard-cure para.

We have on previous occasions urged the advantages of vulcanising rubber under uniform conditions, and testing the vulcanised as against the testing of crude rubbers, for the simple reason alone that practically all rubber is vulcanised in the course of manufacture. It is obvious that it would entail too much work for the method to be applied to the valuation of rubber for purposes of buying and selling; on the other hand, it would be of importance for any plantation company turning out a uniform product, as they are all striving to do, to have a means of ascertaining at first hand how their product compares in practical utility with the products of other estates and with the products of wild rubbers.

The importance of vulcanisation as a means of testing was brought out recently at the discussion of the Society of Chemical Industry on Messrs. Schidrowitz's paper on "The Influence of Formaldehyde on the Properties of the Latex of Funtumia Elastica" (*Journ. Soc. Chem. Industry*, xxvi., No. 24). The tensile strength of the coagulated product is shown to be enormously increased, but if the physical properties of the vulcanised rubber are not similarly enhanced the method has no value except perhaps, as ingeniously suggested by one of the speakers, it should turn out to be a new method of vulcanisation. Even then the paramount importance of the keeping qualities of the rubber so produced require to be investigated, for, as is well known, it is the easiest thing in the world to obtain strength and resiliency in vulcanisation at the expense of keeping qualities, and manufacturers of high-class rubbers will require the properties to be preserved unchanged for at least three years.

After all we do not see that in assessing the value of any new kind of rubber that the methods employed by the most progressive rubber manufacturers in their laboratories have in any way been improved upon by any recently published paper upon the subject. The proof of the pudding is in the eating, and the proof of the rubber is in the vulcanised product.

NITROGLYCERIN AND ITS MANUFACTURE.*

By Lieut.-Col. Sir FREDERIC L. NATHAN, R.A.,
and
WILLIAM RINTOUL, F.I.C.

NITROGLYCERIN was discovered by A. Sobrero in 1847 at Turin. He recognised its explosive properties, but it was not until 1863 that A. Nobel introduced it as a blasting agent in Norway. Owing to several serious accidents in its manufacture and use, its application did not become general until Nobel in 1867 succeeded in absorbing it with kieselguhr, in which form it is known as dynamite. Blasting gelatin, in which soluble nitrocellulose is the absorbent, produced by Nobel in 1875, marked another step in the employment of nitroglycerin as a disruptive explosive, and finally it forms a constituent of ballistite and cordite, both propulsive explosives.

Nitroglycerin is produced by adding glycerin to a mixture of sulphuric and nitric acids. After nitration the nitroglycerin formed separates out from the waste acid, and is submitted to a thorough washing with water and soda solution to remove all traces of acid and unstable bodies. In the early days of its manufacture, the plant was on a very small scale and of simple construction. With the introduction of dynamite, nitroglycerin was made in much larger quantities and the plant was on a bigger scale. Lead vessels were adopted for nitrating and washing, the nitrating apparatus was provided with lead coils through which cold water circulated; compressed air agitation was introduced, and many minor improvements in both plant and process gradually followed. The plant erected at the Royal Gunpowder Factory in 1903 differs in some essential particulars from the plants previously used. Instead of running by gravity the mixture of nitroglycerin and waste acid on the completion of nitration into a separating tank below the nitrating vessel, allowing the separation of the nitroglycerin from the waste acid to take place in this tank, and then running the nitroglycerin again by gravity into a washing tank, the separation is allowed to take place in the nitrator itself, and as the nitroglycerin separates out it is displaced by waste acid admitted at the bottom of the nitrator, down a gutter attached to the top of the nitrator into the pre-wash tank, placed so that its top is very slightly lower than the top of the nitrator. This arrangement much simplifies the plant and obviates the dangers incidental to the use of earthenware cocks. Advantage is taken of the fact that the addition of a small percentage of water to the waste acid after the nitroglycerin has separated out, prevents the formation of further small quantities of nitroglycerin on allowing the waste acid to stand, to do away with the tedious and expensive operation known as "after-separating." Water

* Read before the London Section of the Society of Chemical Industry, February 3rd, 1908.

is added to the waste acid in the nitrator separator, and the acid sent away at once for recovery.

A further improvement, now very general in all modern plants, is the substitution of rubber pipes for earthenware cocks for running off nitroglycerin.

The proportions of sulphuric to nitric acid and of glycerin to the nitrating acid mixture have been varied from time to time. In the early days of manufacture two parts of sulphuric to one of nitric was used, and the proportion of glycerin to mixed acid varied from one-sixth to one-eighth. The more modern practice is to use a mixture of three parts by weight of nitric acid of 1·3 sp. gr. and five parts by weight of sulphuric acid of 1·842 sp. gr., and to nitrate one part by weight of glycerin in every eight parts by weight of the mixture.

The early yield of nitroglycerin varied round 200 per cent; in more modern factories yields averaged about 210 per cent, but an average yield of over 214 per cent was obtained at the Royal Gunpowder Factory over a series of eight years previous to the introduction of the improved plant referred to above; with the introduction of this plant the yield increased to just over 220 per cent. Similar results have also been obtained at other factories using this plant.

Nitrating acid of the composition referred to above contains about forty-seven parts of water which perform no useful function, appearing again in the waste acid. By using an anhydrous nitrating acid of altered composition this water is eliminated, and a much smaller quantity of nitrating acid for a given charge of glycerin can be used, resulting in the production of a smaller quantity of waste acid, the composition of the latter remaining the same as before. As nitroglycerin is absorbed to a certain extent by waste acid (3·7 per cent in one of normal composition) the less the quantity of waste acid the better should be the yield of nitroglycerin. By using Nordhausen acid, an anhydrous acid can be produced, and manufacturing experience has proved that with practically such an acid a yield of 230 per cent of nitroglycerin is obtainable. The absorption of nitroglycerin by waste acid is not merely a case of solution. A secondary reaction also takes place between the sulphuric acid and the nitroglycerin with the production of sulphoglycerin and nitric acid. This reversible reaction speedily attains an equilibrium, so that with a normal waste acid of the total nitroglycerin absorbed, one-half exists as sulphoglycerin and the remainder as nitroglycerin in true solution.

NOTE ON IONIUM.

By W. MARCKWALD and B. KEETMAN.

We have for some time been occupied with experiments to determine the proportion in which radium and actinium are contained in the ores of uranium, and we have thus come upon a hitherto unknown radio-active constituent of these ores, which is obviously identical with the substance, allied to thorium, recently discovered by B. B. Boltwood (*Am. Journ. Sci.*, 1907, [4], xxiv., 370) and O. Hahn (*Ber.*, 1907, xl., 4415). Boltwood proposed the name "ionium" for this substance.

When a uranium ore—we used Joachimsthal pitchblende, crystallised pitchblende from German East Africa, and autunite—is dissolved in nitric acid, the nitrate is converted into sulphate, and filtered from insoluble sulphates (lead, barium, radium), a very strongly active precipitate is separated from the solution by the addition of hydrofluoric acid. It consists chiefly of fluorides of the cerium and yttrium earths, and of thorium. If these fluorides are again brought into solution by evaporating with concentrated sulphuric acid, and then oxalic acid is added to the strongly acid solution, almost all the activity separates with the thorium oxalate. Boltwood precipitated the same substance with thorium by means of thiosulphate.

Boltwood found that the α-radiation of his ionium was much more easily absorbed than that of polonium. Our precipitate also showed this characteristic property. More than two-thirds of its α-radiation is absorbed by aluminium foil of thickness 0·007 mm., while only half of that of polonium is absorbed.

Boltwood found that the ionising power of the substance was to that of the radium separated from the same amount of ore as 8 : 10, while we obtained an average of 7 : 10. The substance does not give an emanation.

There can be no doubt about the identity of the two substances. We have not yet succeeded in separating ionium from thorium. Like thorium oxalate it is dissolved by ammonium oxalate, and again precipitated from the solution by acids. Both thorium and ionium carbonates are soluble in ammonium carbonate.

This last property explains why a substance with such a high emanation power has hitherto escaped discovery. On a large scale only the residues of the Joachimsthal uranium manufacture have been treated for the separation of radio-active substances. But, as our experiments show, these residues are comparatively poor in ionium. Clearly the greater part of the substance goes into solution with the uranium during the process, if to separate it from impurities soda solution is added to the sulphate solution. Therefore the ionium must be looked for, not in the residues, but in the mother-liquor of the manufacture of uranium.

According to the interesting observations of Boltwood and Hahn, ionium seems to be the long-sought intermediate product between uranium or uranium X and radium. We do not intend to go further into this question, which the authors mentioned above have begun to study before us. But we consider that we are justified in continuing our research, the most important results of which we had deduced long before any publication by the above authors had appeared.

We take this opportunity of reporting a surprising circumstance which we observed during the investigation of autunite. This mineral, which is calcium uranium phosphate, and occurs in beautiful crystals, was found to be free from lead when 10 grms. of it were investigated, or at any rate this quantity does not contain one-tenth of a mgrm. of lead. This result, which will be further examined, is of importance because lead is supposed to be the end product of the radio-active transformation of uranium.—*Berichte*, xli., 49.

SOME COMPOUNDS OF TERBIUM AND DYSPROSIUM.

By G. URBAIN and G. JANTSCH.

We have begun a study of the elements of the yttrium group recently isolated by one of us in order to find out what relations exist between the different members of the series, and what differences can be employed to form the basis of processes of separation of these substances, which will be less tedious than those which have been employed to prepare them.

It seemed best to begin this research by studying the simplest compounds, the oxides, chlorides, nitrates, and sulphates. In this article we shall limit ourselves to the description of our first experiments with terbium and dysprosium.

Terbium Peroxide, Tb_4O_7.—Terbium peroxide, which is formed by igniting salts of terbium the acid radicle of which can be eliminated by heat, corresponds exactly to the formula Tb_4O_7, if care is taken to avoid too high a temperature.

At a white heat the oxide, Tb_4O_7, loses oxygen, all of which it does not re-absorb on cooling. For this reason the oxide, which results on igniting the sulphate at 1600°, has a variable composition; the determination of oxygen generally gives numbers which are lower than those required by the formula Tb_4O_7.

If terbium oxalate or hydroxide is heated in a muffle a peroxide is obtained, the percentages of oxygen in which correspond exactly to the above formula.

We convinced ourselves of this by employing a method of determining oxygen which is less liable to error than reduction by hydrogen at a red heat, or the iodometric method previously employed. This method consists in dissolving terbium peroxide by warming it with a titrated solution of ammoniacal ferrous sulphate containing free sulphuric acid in an atmosphere of coal gas. The excess of Mohr's salt is then titrated by potassium permanganate. The numbers found by this method agree with the theoretical number 2·13 to within 1 100 to 2 100.

The establishment of this formula is of great importance for the analysis of compounds of terbium: terbium can be determined as peroxide. Tb_4O_7, if the precautions which have just been described are observed.

Terbium Nitrate, $Tb(NO_3)_3.6H_2O$.—Terbium peroxide is difficultly soluble in nitric acid in the cold. When warmed it dissolves with evolution of oxygen. On evaporating the solution on a water-bath only a syrup is obtained, which on cooling forms a white radiating mass. From nitric acid, containing one-eighth of its volume of water and not used in excess, the nitrate, $Tb(NO_3)_3.6H_2O$, is obtained in the form of colourless monoclinic crystalline needles. This salt is soluble in alcohol. Its aqueous solution is neutral to litmus. In a sealed tube it melts in its water of crystallisation at 89·3°.

Terbium Sulphate, $Tb_2(SO_4)_3.8H_2O$.—The preparation and properties of this salt, which was used for the determination of the atomic weight of terbium, have already been described (G. Urbain, *Comptes Rendus*, 1905, cxli., 521).

The same hydrate is obtained when an aqueous solution containing terbium and sulphuric acid is precipitated with alcohol. It then forms a crystalline powder composed of micaceous lamellæ, insoluble in alcohol and difficultly soluble in water.

Terbium Chloride, $TbCl_3.6H_2O$.—Terbium peroxide dissolves on warming with hydrochloric acid, chlorine being evolved. After the solution has been concentrated until it contains 40 to 45 parts of anhydrous salt in 100 parts of solvent, about one and a-half times its volume of hydrochloric acid is added, and it is left in a sulphuric acid desiccator. The chloride readily gives supersaturated solutions. It is best to induce crystallisation by rubbing the sides of the vessel with a glass rod. The salt thus obtained has the formula $TbCl_3.6H_2O$. It forms colourless transparent prismatic crystals. It is extremely hygroscopic, is soluble in alcohol, and its aqueous solution is neutral to litmus.

Dysprosium does not form a peroxide. Its oxide, Dy_2O_3, does not change in weight when it is heated either in an oxidising or in a reducing atmosphere. Its salts are light yellowish green in colour.

Dysprosium Nitrate, $DyNO_3.5H_2O$.—Under conditions in which terbium nitrate with 6 molecules of water is formed we have always obtained a penta-hydrated dysprosium nitrate.

This nitrate resembles the corresponding bismuth nitrate in every respect, and is almost the same colour. It loses water in a dry atmosphere, and rapidly becomes opaque. It is soluble in alcohol, very soluble in water, and less soluble in water containing nitric acid than in pure water. Its aqueous solution is neutral to litmus. It melts in its water of crystallisation at 88·6°.

Dysprosium Sulphate, $Dy_2(SO_4)_3.8H_2O$. — This salt, which was used for the determination of the atomic weight of dysprosium, has already been described (G. Urbain and Demenitroux, *Comptes Rendus*, cxliii., 598). It resembles very closely the corresponding compound of terbium.

Dysprosium Chloride, $DyCl_3.6H_2O$.—This compound is prepared in the same way as the corresponding chloride of terbium, which it resembles in most of its properties, being, however, less hygroscopic. Its aqueous solution is neutral o litmus.—*Comptes Rendus*, 1908, cxlvi., 127.

THE ATOMIC WEIGHT OF HYDROGEN.*

By WILLIAM A. NOYES.

(Concluded from p. 67).

SECOND SERIES.—*Hydrogen from Sulphuric Acid, Weighed Twice.*

IN this series the hydrogen was weighed in palladium, and also after transfer to the copper oxide tube as described above. In order to increase the quantity of hydrogen and reduce the error, after the water had been removed and the copper re-oxidised, a second quantity, and in one case a third quantity, of hydrogen was introduced, and the water removed. Finally, the reduced copper was transferred to a hard glass tube, and oxidised in a current of oxygen, and the amount of water formed was determined. The oxygen used was partly from the S. S. White Dental Manufacturing Company, and was purified by passing it over red-hot copper oxide and through wash-bottles containing a solution of sodium hydroxide, and over phosphorous pentoxide. In some of the experiments electrolytic oxygen was used.

Several experiments were made to determine the amount of water taken up by the copper oxide in the transfer to the hard glass tube. In a similar manipulation with dry copper oxide there were obtained 2·63, 1·30, 5·32, and 2·45 mgrms. of water. This would correspond to an average error of about one part in 10,000. It has not been thought best to apply any correction for this error, partly because of the uncertainty in its amount, but chiefly because it is probably balanced by small errors in the opposite direction, due to the retention of water by the copper oxide even after several hours at a red heat in a current of oxygen, and to the retention of a trace of water by the walls or lubricant of the copper oxide apparatus. There is good reason, however, for believing that the error from each of these sources is very small.

Weights of Hydrogen (*Second Series*).

	Grms. H.		Mgrms. H.		Corrected H.		Average H.
	CuO tube.	Pd tube.	In T tube	From Cu.	CuO.	Pd.	
1.	3·72469	3·72689	0·15	0·07	3·72462	3·72667	3·72565
2.	3·80383	3·80280	0·17	0·05	3·80378	3·80258	3·80318
3.	3·75898	3·75886	0·18	0·10	3·75888	3·75858	3·75873
4.	2·96309	2·96357	0·05	0·03	2·96306	2·96349	2·96328
5.	2·11437	2·11366	0·08	0·03	2·11434	2·11355	2·11395
6.	3·53126	3·53173	0·19	0·04	3·53122	3·53150	3·53136
7.	3·53963	3·53982	0·19	0·04	3·53959	3·53959	3·53959

Weights of Oxygen and Water (*Second Series*).

	O from loss of CuO.	N.	CO_2.	Water by re-oxidation.	O corrected.	Water.
	Grms.	Mgrm.	Mgrms.	Mgrms.	Grms.	Grms.
1.	29·56469	0·76	0·28	15·26	29·57891	33·30408
2.	30·16645	0·37	2·33	20·25	30·18400	33·98748
3.	29·81141	0·32	0·79	23·28	29·83358	33·59127
4.	23·49099	0·13	0·60	29·61	23·51987	26·48379
5.	—	0·20	1·16	27·65	—	18·89214
6.	27·99401	0·38	0·89	36·36	28·02910	31·56024
7.	28·05652	0·24	0·22	40·13	28·09619	31·63554

Atomic Weight of Hydrogen (*Second Series*).

	From H : O.	From H : H_2O.
1.	1·00765	1·00767
2.	1·00800	1·00799
3.	1·00792	1·00795
4.	1·00792	1·00790
5.	—	1·00795
6.	1·00791	1·00792
7.	1·00785	1·00786
Mean ..	1·00787	1·00789
	± 0·00003	± 0·00003

Mean of all .. 1·00788 ± 0·00002

* From the *Journal of the American Chemical Society*, xxix., No. 12.

Seven determinations were made in this series, but in one of them the weight of the oxygen was lost. The results are given above.

Third Series.—*Hydrogen from Sulphuric Acid Weighed after Conversion to Water by Copper Oxide.*

In this series hydrogen directly from the electrolytic apparatus was passed into the copper oxide bulb and converted into water. The purpose of the series was more especially to determine whether the purity of the hydrogen had been increased by absorption in the palladium. The results of the series are not as concordant as those of the second, but they indicate that the hydrogen directly from the electrolytic apparatus is, if anything, a little lighter and presumably a little more pure than after it has been absorbed in palladium. The results were as follows :—

Weights of Hydrogen and Oxygen (Third Series).

	H by gain of CuO.	H from Cu.	H corrected.	O by loss of CuO.	N.	CO_2.	Water by re-oxidation.
	Grms.		Grms.	Grms.	Mgrm.	Mgrm.	Mgrms.
1.	2·44282	0·03	2·44279	19·34104	0·16	0·10	56·79
2.	2·18741	0·02	2·18739	17·33722	0·10	0·05	25·98
3.	2·75132	0·03	2·75129	21·80908	0·18	0·05	34·60
4.	4·00068	0·06	4·00062	—	—	—	62·31
5.	4·04061	0·04	4·04057	32·04471	0·17	0·06	32·41

Atomic Weight of Hydrogen (Third Series).

	O corrected. Grms.	Water. Grms.	Atomic weight. From H : O.	Atomic weight. From H : H_2O.
1.	19·39757	21·84042	1·00746	1·00746
2.	17·36305	19·55117	1·00784	1·00780
3.	21·84345	24·59389	1·00764	1·00768
4.	—	35·75073	—	1·00803
5.	32·07689	36·11762	1·00772	1·00772
		Mean . ..	1·00767 ± 0·00006	1·00774 ± 0·00006

Mean of all .. .. 1·00771 ± 0·00004

It will be noticed that the amounts of carbon dioxide found are much smaller, owing to the fact that the copper oxide has been freed from it by repeated use. The amount of nitrogen was also smaller, perhaps because of the simpler manipulations involved.

Fourth Series.—*Hydrogen and Oxygen from Sulphuric Acid combined by means of Palladium.*

With the best manipulation which it has been possible thus far to secure, the use of copper oxide involves several sources of small constant errors. It is hoped that these errors do not, in the aggregate, exceed one part in 10,000, but it seemed very desirable to find some radically different method which should avoid the use of copper oxide. Such a method consists in absorbing hydrogen in palladium and converting it into water by means of oxygen. This method has already been used by Keiser (*Am. Chem. Journ.*, xx., 733). but his method of manipulation compelled him to use comparatively small amounts of hydrogen, and the degree of concordance which he was able to secure was not such that his value for the atomic weight of hydrogen can be used to decide between Morley's value and that found here.

The problem seemed at first a very simple one, but several months were spent in fruitless experiments before a satisfactory method of manipulation was found.

The 360 grms. of palladium foil previously used were placed in a somewhat wider tube and were kept from direct contact with the glass by means of small glass beads strung on platinum wires. The stopcock at one end of the tube was replaced by a tube having a capacity of about 50 cc. At the beginning the palladium tube was heated and charged with hydrogen and partially exhausted several times to remove moisture. It was then heated to 380°—400° and exhausted until the hydrogen showed a residual pressure of 0·50 to 0·70 mm. as measured by the McLeod gauge. At this pressure and temperature 360 grms. of palladium retain only 2—3 mgrms. of hydrogen, and the amounts of hydrogen given out for small changes of pressure are as follows :—

0·40 to 0·50 mm.	0·11 mgrm. H
0·50 ,, 0·60 ,,	0·10 ,,
0·60 ,, 0·70 ,,	0·094 ,,
0·70 ,, 0·80 ,,	0·087 ,,
0·80 ,, 0·90 ,,	0·080 ,,
0·90 ,, 1·00 ,,	0·073 ,,
3·90 ,, 4·00 ,,	0·044 ,,
16·90 ,, 17·00 ,,	0·020 ,,

A change of temperature of 10° for pressures less than 1 mm. corresponds to a change of 0·03 mgrm. in the amount of hydrogen retained. At the end of an experiment it was easy to bring the apparatus to a condition of temperature and pressure closely approximating that at the beginning, and by means of the table a correction of sufficient accuracy could be applied.

After exhausting, and measuring the temperature and pressure as described, the apparatus was allowed to cool, rinsed with distilled water, wiped, placed on the balance, and on the following morning it was weighed. It was then charged with hydrogen (about 2·3 grms.) and weighed again on the morning of the third day. The apparatus was then connected with the oxygen side of the electrolytic generator. The palladium tube was inclined so that the water formed ran down into the receptacle at the end. The oxygen entered rapidly for a few minutes, but the heat generated soon caused the pressure of the hydrogen to increase and check the current. The oxygen then continued to enter slowly, with the stopcock partly closed, for two or three hours. After that the rate at which the oxygen was taken changed quite suddenly, so suddenly that the first time the experiment was tried the electrolyte was drawn over and the electrolytic apparatus was broken. From this time to the end the entrance of the oxygen was regulated by the stopcock and was allowed to enter as rapidly as it was thought desirable to run the generator. More than enough oxygen to combine with the hydrogen present was easily introduced. On the fourth day, after weighing, the apparatus was charged again with hydrogen.

On the fifth day the manipulation varied. In some cases oxygen was admitted in excess as on the third day. In other cases, as the end of the oxidation of the hydrogen approached, the apparatus was weighed roughly at intervals and the admission of the oxygen was stopped while 5—10 mgrms. of hydrogen remained unoxidised. By this method of manipulation a day was saved. On the sixth day, or, when an excess of oxygen was admitted, on the fifth, a small excess of hydrogen was admitted. It was necessary to wait till the following day before weighing.

On the sixth or seventh day, according to the method of manipulation chosen, the water and excess of hydrogen were removed and the apparatus brought back to a condition for the beginning of a new experiment. A receptacle similar to that described on p. 66 was used for the water. On account of the hydrogen which accumulated rapidly in the bulb with the water and stopped the current of water vapour, it was found desirable to give the bulb a capacity of about 100 cc. Any nitrogen present was, of course, carried over with the first portions of the water vapour and hydrogen, and this part of the gas was collected and analysed separately. At the close of the removal of the water, the receptacle for the water was replaced by a phosphorous pentoxide tube, which permitted of a free connection between the palladium tube and the pump for the measurement of the residual pressure. It was necessary to heat the palladium tube at least two hours in the electrical air-bath to secure constant conditions for the measurement of the residual pressure. This was not understood

in the earlier determinations of this series, and may be one reason why some of the results are not very satisfactory.

In the results which follow, the amounts of nitrogen and carbon dioxide are given as an indication of the magnitude of the errors which may have been occasioned by traces of these gases or by leakages, but no correction for these gases has been applied.

Theoretically, the weight of the apparatus at the end of an experiment should be the same as at the beginning. Practically, it was almost always heavier because of the retention of a small amount of water. When the hydrogen was allowed to accumulate in the receptacle for water the moisture would condense in the connecting tubes and stopcocks, and if allowed to remain for a short time in contact with the lubricant of the stopcock, could not be entirely removed. In some cases minute drops of water could be seen within the bore of the stopcock, and these would not evaporate during any reasonable length of time. The gain in weight of the apparatus during the experiment was, accordingly, assumed to be due to water which had been retained and was added to the weight of water found directly. In cases where condensation was avoided this amount of water was very small or even became negative. (See the following series.)

Weights of Hydrogen and Oxygen (Fourth Series).

	H.	Corrected for changes of *t* and P.	H recovered.	H corrected.	N.	CO_2.	O.
	Grms.	Mgrm.	Mgrms.	Grm.	Mgrm.	Mgrm.	Grms.
1.	2·31840	−0·05	39·19	2·27916	0·48	0·02	18·08455
2.	4·13630	−0·06	8·90	4·12734	0·50	—	32·76527
3.	4·18248	+0·24	7·16	4·17556	0·52	0·02	33·13449
4.	4·19599	−0·51	2·02	4·19346	0·15	0·16	33·27384
5.	2·31593	−0·01	8·46	2·30746	—	—	18·30863
6.	4·60148	−0·23	4·33	4·59692	0·11	0·08	36·48543
7.	4·63931	+0·14	3·20	4·63625	0·07	0·07	36·79354
8.	4·57292	+0·18	0·36	4·57274	0·02	0·28	36·28696

Weights of Water and Atomic Weight of Hydrogen.

	Water. Grms.	Water retained. Mgrms.	Water corrected. Grms.	Atomic weight. From H : O.	Atomic weight. From H : H_2O.
1.	20·29807	63·21	20·36128	1·00823	1·00830
2.	36·87182	18·61	36·89043	1·00774	1·00780
3.	37·30667	1·20	37·30787	1·00818	1·00821
4.	37·46202	2·51	37·46453	1·00822	1·00831
5.	20·61671	−3·14	20·61357	1·00825	1·00839
6.	41·07653	5·09	41·08162	1·00795	1·00797
7.	41·41452	14·53	41·42905	1·00806	1·00808
8.	40·85460	3·74	41·85834	1·00813	1·00817
			Mean	1·00809 ± 0·00004	1·00815 ± 0·00005

Mean of all .. .. 1·00812 ± 0·00003

Fifth Series.—*Hydrogen and Oxygen from Barium Hydroxide, combined by Means of Palladium.*

The manipulation in this series was essentially the same as in the fourth series. The series has much greater value than the former one, partly as shown by the concordance of the results, partly because the processes of manipulation had been more thoroughly mastered, and partly because the electrolyte used gives a greater probability of purity for the hydrogen. In those experiments in which oxygen was introduced last, a small quantity was left in the bore of the three-way stopcock and was usually found in the subsequent analysis of the first portions of gas removed. In one experiment of this series only one-half the quantity of hydrogen was used, and too much oxygen was admitted by mistake. This so complicated the manipulation that the experiment was unsatisfactory and it has been omitted from the table. It gave the values 1·00814 and 1·00823.

Weights of Hydrogen and Oxygen (Fifth Series).

	H.	Corrected for changes of *t* and P.	H recovered.	H corrected.	N.	CO_2.	O.	O.
	Grms.	Mgrm.	Mgrms.	Grms.	Mgrm.	Mgrm.	Mgrm.	Grms.
1.	4·61443	−0·07	2·56	4·61180	0·11	0·17	—	36·60909
2.	4·62877	0·00	5·19	4·62358	0·08	0·03	0·13	36·69575
3.	4·60386	−0·02	5·31	4·59853	0·22	0·00	1·31	36·50484
4.	4·56300	+0·04	4·72	4·55832	0·06	0·00	0·29	36·17887
5.	4·21188	−0·04	7·85	4·20399	0·11	0·00	0·11	33·37000

Weights of Water and Atomic Weight of Hydrogen,

	Water. Grms.	Water retained.	Water corrected. Grms.	Atomic weight. From H : O.	Atomic weight. From H : H_2O.
1.	41·21934	1·71	41·22105	1·00779	1·00779
2.	41·30740	9·07	41·31647	1·00798	1·00806
3.	41·09872	3·40	41·10212	1·00776	1·00780
4.	40·74186	−2·82	40·73904	1·00795	1·00790
5.	37·57132	6·04	37·57336	1·00782	1·00786
			Mean	1·00786 ± 0·00003	1·00788 ± 0·00003

Mean of all .. .. 1·00787 ± 0·00002

The mean of the four series, giving them equal weight, is 1·00787 from the hydrogen and oxygen, and 1·00791 from the hydrogen and water. The second and fifth series have, however, much greater weight than the third and fourth, and when we consider, further, that there was probably a trifling loss of water, especially in the third series, the value 1·00787 seems to be the most probable result which can be calculated from the work.

(The mean of the results of the twenty-three determinations in which the hydrogen and oxygen were weighed is 1·00791 and the mean of the twenty-five determinations in which the hydrogen and water were weighed is 1·00794. The mean of all, considered as a single series of forty-eight determinations, is 1·00793 ± 0·00002).

It has seemed of interest to recalculate Morley's results on the oxygen basis for comparison with the result here given.

Atomic Weight of Hydrogen (Morley's Results).

1.	1·00765	1·00778
2.	1·00751	1·00766
3.	1·00768	1·00774
4.	1·00755	—
5.	1·00773	1·00750
6.	1·00773	1·00778
7.	1·00777	1·00786
8.	1·00764	1·00761
9.	1·00759	1·00752
10.	1·00752	1·00737
11.	1·00746	1·00734
12.	1·00744	1·00771
Mean ..	1·00761 ± 0·00002	1·00763 ± 0·00003

Mean of all .. 1·00762 ± 0·00002

The difference between this result and that given above is greater than can be accounted for on the basis of accidental errors. While the average of the results of the best determinations by either observers approaches more nearly to the result of this investigation than to Morley's value, it does not seem justifiable to calculate a mean on such a basis. For reasons which will be given in a later paper the most probable value which we can get at the present time seems to be the average between Morley's value and that here given. That average is *1·00775*. Morley's value and my own each differ from this by one part in 8000.

Change in Weight of the Hydrogen when Converted into Water.

As was stated in the introduction, one purpose of this investigation was to secure, if possible, some evidence of a change of weight which might occur in a reaction in which a large amount of energy is dissipated. In twenty-five experiments the same hydrogen was weighed, first, as absorbed in palladium and, second, after conversion into water by means of the copper oxide. The results were as follows :—

Gain of CuO.	Loss of Pd.	Difference (mgrm.).
1·04216	1·04295	+0·79
1·46493	1·46642	+1·49
0·96114	0·96231	+1·17
1·51279	1·51296	+0·17
1·17961	1·17973	+0·12
1·22273	1·22268	−0·05
1·13563	1·13541	−0·22
1·30184	1·30150	−0·34
1·22851	1·22699	−1·52
0·99563	0·99600	+0·37
1·24243	1·24270	+0·27
1·24639	1·24754	+1·15
1·52682	1·52706	+0·24
0·95151	0·95207	+0·56
1·98130	1·98053	−0·77
1·82248	1·82205	−0·43
2·04840	2·04816	−0·24
1·71048	1·71042	−0·06
1·96621	1·96648	+0·22
0·99685	0·99707	+0·22
2·11434	2·11335	−0·79
2·20439	2·20472	+0·33
1·32683	1·32678	−0·05
2·07207	2·07281	+0·74
1·46752	1·46678	−0·74
36·72299	36·72562	+2·63

An examination of these results shows that in fourteen experiments the hydrogen as weighed in the palladium appeared heavier, while in eleven experiments the hydrogen after conversion into water appeared heavier. The average difference between the two weights of a given quantity of hydrogen was 0·52 mgrm. or one part in 3000, while the average amount by which the hydrogen as weighed in the palladium appeared heavier was 0·11 mgrm., or one part in 14,000. It is clear that these results do not justify any conclusion either way with regard to a change in weight of the hydrogen during the reaction other than that if any change of weight occurs it must be very small. It seems scarcely possible that a change of so much as one part in 10,000 of the weight of the hydrogen takes place. It is possibly of interest to note that, so far as the results furnish any indication whatever, they point toward a trifling loss of weight, a result which would agree with Landolt's elaborate study of the question (*Zeit. Physik. Chem.*, lv., 589). It is hoped that this problem may be taken up again by a method capable of giving more accurate results.

Lothar Meyer Memorial. — The Council of the Chemical Society has decided to make a donation of £10 to the Lothar Meyer Memorial Fund. Many old pupils and admirers of the author of "Die Modernen Theorien der Chemie" may be desirous of contributing to this Memorial, and the Treasurer will be glad to receive, at an early date, subscriptions from Fellows and others to the Fund. Cheques, &c., should be made payable to Dr. Alexander Scott, crossed "Lother Meyer Memorial Fund A/c," and sent to the Treasurer, Chemical Society, Burlington House, W.

THE INFLUENCE OF LIGHT AND OF COPPER ON FERMENTATION.*

By J. E. PURVIS, M.A., St. John's College,
and
W. A. R. WILKS, B.A., Gonville and Caius College.

The action of light on various species of Saccharomyces has been studied by different observers, and amongst these the researches of Kny and Lohmann are of some importance (Duclaux, "Traité de Microbiologie," iii., p. 289; Kny, *Ber. d. Botan. Gesells*, 1894, Heft 3; Lohmann, "Inaug. Dissertation," Rostock, 1896).

The former placed the yeast in culture solutions in flat dishes, and exposed a part to the light of five gas flames, whilst the other part was in the dark, the heat rays being removed by filtering the light through water. His conclusion was that the *budding* of *S. Cerevisiæ* took place in moderate light with the same activity as in darkness.

Lohmann studied the action of both sunlight and the arc. He seeded cultures of *S. Cerevisiæ* on wort gelatin on glass slips, and exposed them to the action of a powerful arc lamp for eight hours. Above a temperature of 18° C. he found that the budding was retarded in the cultures subjected to the light. The same yeast was seeded on agar-agar plates, and exposed to the action of sunlight, when the yeast was killed after several hours. He also noticed that even diffused daylight had a retarding influence on the budding of the cultures, but that this only occurred after prolonged exposure to the light.

The influence of light and various spectral colours on the sporulation of Saccharomyces has been studied by Purvis and Warwick (*Proc. Camb. Phil. Soc.*, xiv., Part 1, p. 30). They observed that the red rays accelerated the formation of spores more quickly than white light and more quickly than when the development took place in the dark: that the green rays retarded the development: that the blue and violet rays retarded the sporulation still more: and that the ultra-violet rays were still more effective, and that they influenced the vitality of the cells detrimentally when the latter were exposed to the influence for some time.

It appeared to be of some interest to study the effect of light during a normal fermentation of hopped wort and other fermentable solutions, and the following notes describe the results of a comparative study of the influence of light and of various spectral colours upon fermentation when conducted in (*a*) unsterilised copper vessels, (*b*) sterilised glass vessels, and (*c*) in unsterilised glass and copper vessels. The effects of the influences were traced in determinations of the optical activity, the copper oxide reducing power, the nitrogen content, the acidity, and the specific gravity of the distilled fermented solution (and therefore the amount of alcohol produced). The temperature of the fermenting wort was noted from time to time.

Description of the Apparatus.

In the first series of experiments there were four copper vessels, and one side of three of these was replaced (1) by ordinary glass, (2) by red glass, (3) by an ammoniacal solution of copper sulphate; whilst, for the experiments in the dark, a copper vessel of the same size and volume as the first three was used. As regards the first three vessels they were arranged with the glass sides facing a fairly large incandescent light, the red glass copper vessel a little further away than the other three, and they were covered with loosely fitting lids. The four vessels, and the central light, were covered with thick black cloth so as to exclude any external light. The time during which the fermentation was allowed to proceed varied from four to seven days.

The nitrogen determinations were by Kjeldahl's method; the specific gravities by a specific gravity bottle; the optical activity by a three shadow polariscope; the copper

* *Proceedings of the Cambridge Philosophical Society*, xiv., Part 4.

oxide by reduction of the oxide by hydrogen in small glass tubes and weighing the copper produced. In determinations of the acidity, 50 cc. of one of the fermented solutions were made up to a definite volume, 4 cc. of litmus solution added, and N 10 alkali until, as far as could be roughly judged, neutralisation was complete; 50 cc. of this solution was then placed in a Nessler cylinder. Fifty cc. of the other solutions made up to the same volume as before were then neutralised until, on taking out 50 cc., the same tint was observed as the original 50 cc. The method was also used in the nitrogen determinations, and it gave most satisfactory results.

As regards the temperature observations, we only give the details in the second series of experiments, and merely note the average temperatures in the others. In the determination of the other constituents we give the mean of two separate experiments.

Sterilised hopped wort was used in the series of Experiments A and C: whilst a specially prepared fermentable solution was used in the series of Experiments B.

Details of the Experiments.

A.

I. Equal volumes of hopped wort were placed in the four vessels and allowed to ferment under the influence of ordinary English yeast. The analysis of the unfermented wort gave: copper oxide reducing power of 20 cc. of a 5 per cent solution = 0·189 grm. Cu. The optical activity at 15° C. for 100 per cent wort = +17·68°.

The N. content; 50 cc. of N/10 H_2SO_4 were used, and 42·7 cc. of N/10 NaHO were required to neutralise excess after Kjeldahling 10 cc. of the wort.

The temperature on starting the fermentation was 15·5° C., and the average temperatures between April 24 at 2 p.m. and April 27 at 9.30 a.m were :—

Dark	=22·6° C.	Red	=22·9° C.
White	=23·2	Blue	=22·4

After the fermentation the following results were obtained.

1. Optical activity for 100 per cent solution at 15° C.:—

Dark	= +14·10°	Red	= +8·08
White	= +7·98	Blue	= +7·86

The number for the dark is high and comparable with that of the original wort. It may be the result of the action of acidifying organisms growing very rapidly; and at the rather low starting temperature the resultant acid dissolving a little copper of the vessel, and thereby influencing detrimentally the growth of the yeast. In the remaining experiments the wort was previously warmed to a temperature higher than 15° C.

2. Copper oxide reducing power—20 cc. of a 5 per cent solution gave :—

Dark ..	=0·1580 grm. Cu.	Red ..	=0·1930 grm. Cu.
White..	=0·1345	Blue..	=0·1895

It is noticeable that the copper oxide reducing power is comparable with the optical activity, with the exception of the white light. The discrepancy is not quite explicable, for in the remaining experiments, the white light ones are quite normal and comparable.

3. Specific gravity :—

Dark.	=999·49	Red..	=992·52
White	=992·22	Blue	=993·99

The specific gravities show differences which are not so marked as in the later experiments; and this may be due to the rise in temperature in the red being much more rapid than in the blue and the dark, owing to the absorption of the red rays; the bacteria have then much less chance of active development in the blue and in the dark than in the red.

The acidities and the nitrogen contents were not determined.

II. The following is the analysis of the unfermented wort :—

The optical activity for 100 per cent solution = +24·34°.

The copper oxide reducing power of 20 cc. of a 5 per cent solution = 0·222 grm. Cu.

The nitrogen content; 25 cc. N 10 H_2SO_4 were used, and 13·7 cc. of N/10 NaHO were required to neutralise the excess after Kjeldahling 10 cc. of the wort.

The wort was pitched on April 30 at 4 p.m., and as an example of the changes in temperature during the fermentation, the following table gives details of the readings in °C. :—

	Dark.	White.	Red.	Blue.
May 1, 10 a.m... ..	22·25	22·25	22·75	22·00
,, 2 p.m... ..	26·75	26·00	27·25	26·00
May 2, 10.30 a.m. ..	23·25	22·75	23·50	23·25
,, 4 p.m... ..	24·75	23·50	23·75	24·25
May 3, 11 a.m... ..	23·00	23·00	23·75	23·50
,, 3 p.m... ..	23·60	24·00	24·75	24·10
May 4, 9 a.m... ..	22·75	22·25	23·50	23·00

The average temperatures throughout the fermentation were :—

Dark	=23·8° C.	Red	=24·2° C.
White	=23·4°	Blue	=23·7°

The higher temperature is the red as compared with the others is to be noted.

The fermentations were stopped on May 4 at 9.30 a.m. The one in the red and the dark had marked ethereal odours. The white was less so, and the blue hardly at all. The following results after the fermentations were obtained :—

1. The optical activity for 100 per cent solutions at 15° C.

Dark	= +7·86°	Red	= +7·32
White.. ..	= +6·94	Blue	= +6·54

2. The copper oxide reducing power in 20 cc. of a 20 per cent solution gave :—

Dark..	=0·1170 grm. Cu	Red ..	=0·1015 grm. Cu
White.	=0·0980	Blue..	=0·0860

3. The specific gravity gave :—

Dark	=987·40	Red	=987·11
White	=987·39	Blue	=987·13

4. The nitrogen content; 10 cc. of each of the fermentations were used in the Kjeldahl method and 25 cc. N/10 acid used to neutralise the NH_3 distilled. The number of cc. of N/10 acid required to neutralise the NH_3 were :—

Dark	=7·95 cc.	Red	=7·85 cc.
White	=8·00	Blue	=7·95

These numbers appear to prove that there is little or no effect upon the nitrogen assimilation or solution.

5. The acidity. The following numbers represent the number of cc. of N/10 alkali used in the neutralisation.

Dark	=13·6 cc.	Red	=15·1 cc.
White	=13·8	Blue	=13·7

III. The following is the analysis of the unfermented wort :—

Optical activity for 100 per cent solution = +6·96°.

The copper oxide reducing power for 20 cc. of a 20 per cent solution = 0·197 Cu.

The nitrogen content; 25 cc. of N/10 H_2SO_4 were used and 21 cc. of N/10 NaHO were required to neutralise the excess after Kjeldahling 10 cc. of the wort.

The wort was pitched on May 6, and the average

temperatures between May 7 at 10 a.m. and May 11 at 9 a.m. were :—

Dark .. .. = 23·8° C. Blue .. .. = 23·9° C.
White .. .. = 24·0

The fermentation in the red was not continued owing to an accident.

The following numbers give the results of the analysis of the various fermentations :—

1. Optical activity for 100 per cent solutions at 15° C.

Dark . .. .. = +2·10° Blue.. .. .. = +2·31°
White .. .. = +2·37

2. Copper oxide reducing power in 20 cc. of 50 per cent solutions :—

Dark.. = 0·0725 grm. Cu. Blue . = 0·0660 grm. Cu.
White. = 0·0970

3. Specific gravity :—

Dark .. .. .. = 997·88 Blue .. .. .. = 997·94
White. .. .. = 998·23

4. The nitrogen content ; 10 cc. of each fermentation was Kjeldahled, and the NH_3 distilled into 25 cc. of N/10 acid. The following numbers represent the amount of N/10 alkali used to neutralise excess of acid :—

Dark .. .. = 22·95 cc. Blue .. .. = 23·37 cc.
White .. .. = 23·60

5. The acidity. The following numbers represent the amounts of N/10 alkali required to neutralise 50 cc. of each of the various fermentations :—

Dark .. .. = 7·77 cc. Blue. .. .. = 6·20 cc.
White .. .. = 12·47

The small development of acidity in the dark and blue is very marked.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, January 16th, 1908.

Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

(Concluded from p. 69).

7. "*The Formation and Reactions of Imino-compounds.* Part VI. *The Formation of Derivatives of Hydrindene from o-Phenylenediacetonitrile.*" By Charles Watson Moore and Jocelyn Field Thorpe.

When *o*-phenylenediacetonitrile (I.) is warmed in alcoholic solution containing a trace of sodium ethoxide, it is completely converted into *α-cyano-β-iminohydrindene* (II.), which can be hydrolysed to *α-cyano-β-hydrindone* (III.).

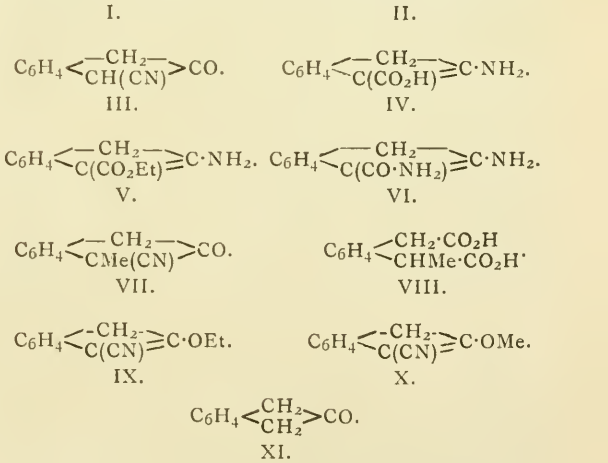
α-Cyano-*β*-iminohydrindene (II.) is a neutral imino-compound, which is hydrolysed by dilute acids, and does not evolve nitrogen with nitrous acid. If, however, the nitrile group is replaced by carboxyl, carboethoxyl, or the carboxylamino-group, the compounds formed are true bases. Thus, *2-aminoindene-3-carboxylic acid* (IV.), *ethyl 2-aminoindene-3-carboxylate* (V.), and *2-aminoindene-carboxyl amide* (VI.) are all bases, which are not hydrolysed by dilute acids, and evolve free nitrogen when treated with nitrous acid. There is no evidence that these compounds are capable of reacting in the imino-form.

α-Cyano-*β*-hydrindone (III.) gives a well-defined *phenylhydrazone*, and on methylation yields *α-cyano-α-methyl-β-hydrindone* (VII.), which gives *phenyleneaceticpropionic acid* (VIII.) on hydrolysis. When, however, the ketone is treated with sodium ethoxide and ethyl iodide, the O-ethyl derivative, *3-cyano-2-ethoxyindene* (IX.), is alone produced.

α-Cyano-*β*-hydrindone (III.) reacts also as a phenol, since it can be readily alkylated by alkyl sulphates, yielding, with methyl sulphate, *3-cyano-2-methoxyindene* (X.) and with ethyl alcohol and sulphuric acid, 3-cyano-2-ethoxyindene (IX.), identical with the compound prepared by the alkylation of the ketone with sodium ethoxide and ethyl iodide. The constitution of these salts is shown by their hydrolysis with dilute acids to *α*-cyano-*β*-keto-hydrindene.

It is therefore probable that groups greater than Me and CN cannot attach themselves to the *α*-carbon atom of *β*-hydrindone or *β*-iminohydrindene, and it is suggested that the term "stearic inhibition" should be applied to this phenomenon rather than "stearic hindrance."

β-Hydrindone (XI.) can be prepared by distilling with steam a solution of 2-aminoindene-3-carboxylic acid (IV.) in dilute sulphuric acid. This substance is quite stable when pure, and does not show any tendency to pass into a brown resin as stated in the literature.



8. "*Valency.*" By John Albert Newton Friend.

The author suggested a new theory of valency by means of which many reactions receive explanations not forthcoming from the usually accepted theory. The theory was also considered in its relation to that of Werner.

9. "*The Esterification Constants of the Normal Fatty Acids.*" By John Joseph Sudborough and James Mylam Gittins.

The esterification constants of some sixteen of the more common normal fatty acids, from formic to stearic acid, have been determined.

The value $E^{15°}_{MeOH}$ for formic is 1124 ; acetic, 104 ; propionic, 92 ; and from butyric to stearic acid the value remains nearly constant, varying from about 50 to 54.

10. "*The Anomalous Behaviour of the Hydrogen Electrode in Solutions of Lead Salts and the Existence of Univalent Lead Ions in Aqueous Solutions.*" By Henry George Denham and Arthur John Allmand.

An attempt has been made to measure the hydrolysis of lead salts by the hydrogen electrode, but results were obtained which were far higher than those recorded by Ley (*Zeit. Physik. Chem.*, 1899, xxx., 193), and it was also noticed that many hours were required for the electrode to give a constant potential. This has been proved to be due to the reaction $Pb^{\cdot\cdot}+H \rightarrow Pb^{\cdot}+H^{\cdot}$ occurring at the platinum electrode.

The existence of plumbous acetate in aqueous solutions has been conclusively proved by carrying out an experiment of the type described by Richards, Collins, and Heimrod (*Zeit. Physik. Chem.*, 1900, xxxii., 321) for copper, and by Bose (*Zeit. Elektrochem.*, 1907, xiii., 477) for silver. In hot solution, lead reduces lead acetate to plumbous acetate, but the reaction is reversed in the cold, crystalline lead being deposited in the cold parts of the apparatus. The ionic reaction is evidently—

$$Pb^{\cdot\cdot}+Pb \rightleftharpoons 2Pb^{\cdot}.$$

It has also been proved that a rod of lead, immersed in a molar-normal solution of lead acetate, the upper part of which is kept hot by a steam-jacket, forms a thermo-electric cell. A weak thermo-current flows from the hot solution to the colder below, and, after a week, definite traces of spongy lead may be recognised at the junction of the hot and cold solutions.

11. "*Amphoteric Metallic Hydroxides.*" (Part I.). By John Kerfoot Wood.

The author has investigated the amphoteric character of the hydroxides of arsenic and aluminium. Arsenic hydroxide is a very feeble base, the basic constant being of the dimensions 1×10^{-14}. The acidic constant, as found by the saponification method, has a value of $6{\cdot}3\times10^{-10}$, and an N/10 solution of sodium metarsenite is hydrolysed to the extent of 1·4 per cent at 25°. The dissociation constant of arsenious acid, as found by the conductivity method, has a value of $26{\cdot}5\times10^{-10}$.

Aluminium hydroxide is a weak base. The chloride is hydrolysed to the extent of about 4 per cent at 25° and is probably transformed into a basic chloride having the formula $Al(OH)Cl_2$. Sodium metaluminate in N/10 solution is hydrolysed to the extent of about 35 per cent at 25°, the acidic constant of aluminium hydroxide being $6{\cdot}3\times10^{-13}$.

12. "*The Use of Pyridine Bases as Halogen Carriers.*" By William Ernest Cross and Julius Berend Cohen.

The authors have shown that the process of halogen substitution in the case of aceto-*p*-toluidide and other amides is preceded by the formation of additive compounds (*Proc.*, 1907, xxiii., 326), but attempts to effect substitution in a similar manner by means of the additive compounds of the pyridine bases with bromine failed.

The result, however, suggested the possibility of employing these bases as halogen carriers, an anticipation which has been confirmed by the following experiments:—

Chlorobenzene.—Chlorine was passed into 50 grms. of benzene containing a few drops of pyridine, and the mixture was warmed to 50°. The action proceeded rapidly with evolution of hydrogen chloride. The product was shaken with alkali, dehydrated, and distilled. Some unchanged benzene and a little dichlorobenzene were separated. The yield of pure chlorobenzene was 30 grms.

Chlorotoluenes.—The chlorination proceeds at the ordinary temperature. From 43 grms. of toluene, 25 grms. of mixed chlorotoluenes were obtained, b. p. 150—165°, together with a few grms. of higher boiling products.

Bromobenzene.—A few drops of pyridine were added to a mixture of 50 grms. of benzene and 120 grms. of bromine, which were warmed to 25° in the water-bath. The action proceeds vigorously with the evolution of hydrogen bromide. The temperature was finally raised to 65—70°. The crude product, which boiled at 148—158°, amounted to 60 grms. The same result was produced with quinoline and isoquinoline.

Dibromobenzene.—The *p*-dibromo-compound was obtained in a similar manner. From 33 grms. of bromobenzene, 20 grms. of the para-compound, m. p. 87°, were obtained, the remainder being unchanged bromobenzene. No ortho-compound was detected.

Bromotoluene.—Fifty grms. of toluene yielded 87 grms. of bromotoluene, b. p. 178—182°.

4-Chloro-1-bromotoluene.—Fifty-five grms. of *p*-chlorotoluene gave 56 grms. of chlorobromotoluene, b. p. 220—235°, and a small quantity of lower and higher boiling products.

α-Bromonaphthalene.—The α-compound was prepared by dissolving 25 grms. of naphthalene in 100 cc. of chloroform, and adding 36 grms. of bromine and a few drops of pyridine. The mixture was left in the cold for twenty-four hours. After purification, 35 grms. of α-bromonaphthalene were obtained, b. p. 276—278°.

13. "*Decomposition of Hyponitrous Acid.*" By Edward Divers.

By suddenly drenching dry silver hyponitrite or mercurous hyponitrite at a temperature but little below 30° with a mineral acid, not greatly diluted in the case of hydrochloric acid or sulphuric acid, and only sufficiently so in the case of nitric acid to avoid inducing its oxidising action, Rây and Gañguli (*Trans.*, 1907, xci., 1866) have obtained nitric acid and nitrogen as products of decomposition, in place of much of the nitrous oxide which was to be expected. This interesting observation throws much light on the nature of the decomposition of silver and mercury hyponitrites by heat. These authors, indeed, suggest that the presence of mineral acids has a "specific directive influence" in determining the form of the decomposition, but that is a notion without evident support. That sulphuric acid should be less effective in bringing about the decomposition is sufficiently accounted for by the fact that the comparative insolubility of silver and mercurous sulphates greatly impedes the action of this acid on the hyponitrites and the rise of temperature which attends it.

Through Rây and Gañguli's observations, we are at length in possession of much knowledge of what the products are when hyponitrous acid decomposes, without explosion, by the heat generated in liberating it from its salts. Since hyponitrous acid yields only nitric acid and nitrogen (water and nitrous oxide being here negligible), whilst silver hyponitrite or mercurous hyponitrite yields, besides these, much nitric oxide and some nitrous acid or nitric peroxide, we can now see that production of the latter substances is due to the unstable oxidised silver or mercury. Writing hyponitrous acid as H_2O,N_2O, and its silver salt as Ag_2O,N_2O, we see that $5N_2O$ becomes $4N_2+N_2O_5$, the water remaining unchanged in the former case, whereas the silver oxide in the latter case is reduced to metal, whilst its oxygen becomes active. Hence we obtain the two equations—

$$5H_2O_2N_2=4H_2O+4N_2+2HNO_3$$

and—

$$3Ag_2O_2N_2=4Ag+2N_2+2AgNO_3.$$

Similarly, the production of nitric oxide and peroxide is referable to the reducibility of oxidised silver or mercury, and could only come from hyponitrous acid through a highly improbable cumulative resolution of nitrous oxide.

Royal Society of Arts.—His Majesty the King, who is Patron of the Society of Arts, has granted permission to the Society to prefix to its title the term "Royal," and the Society will consequently in future be known as the "Royal Society of Arts."

OBITUARY.

PROFESSOR W. A. SHENSTONE, F.R.S.

We regret to have to announce that the death has recently occurred of Prof. W. A. Shenstone, the Senior Science Master at Clifton College, Bristol. The late Professor took an active part in the movement which had in view the reform of methods of teaching science, and his "Text-Book of Inorganic Chemistry" and "Course of Chemistry" are recognised as authoritative books on modern methods of putting before beginners the elements of chemistry in the most scientific and logical way. Other books written by Professor Shenstone include an excellent "Life of Liebig," in the Century Science Series, and "The Methods of Glass Blowing," while he contributed many articles on chemical subjects to scientific magazines. Shenstone conducted some valuable investigations on the preparation of ozone, and succeeded in obtaining far larger yields than had before been held to be possible. His researches on the use of fused silica for making apparatus were attended with a considerable measure of success, and he acted as technical adviser to the firm of Johnson, Matthey, and Co., Ltd., who have put upon the market vessels of all shapes to take the place of those made of glass. Fused silica vessels are transparent and practically unbreakable by sudden changes of temperature. They are not attacked by acids (except hydrofluoric acid), have a high melting-point, and are harder than glass; they have found an extensive application in many important laboratories, especially for fine quantitative work.

NOTICES OF BOOKS.

Immunochemistry. By Svante Arrhenius. London: Macmillan and Co., Ltd. New York: The Macmillan Company. 1907.

This book gives a detailed summary of a series of lectures delivered by the author at the University of California, in Berkeley, California, in the summer of 1904. In these lectures Professor Arrhenius described the results obtained by the application of physical chemistry to the toxins and antitoxins, and gave a review of the experimental material which has been collected relating to the chemistry of immunity. Adopting the view of the chemical school of physiologists, who believe that the effects of antitoxins are of a purely chemical nature, he has brought together the numerous quantitative results which have been obtained, especially by Madsen and his fellow-workers, and has shown that, as far as has yet been observed, all the facts which have been accumulated agree with the known laws of physical chemistry for ordinary chemical compounds. The whole tone of the work is stimulative to further research, and the author has produced a convincing exposition of the subject, showing where uncertainties still exist, and in what directions more work is most urgently wanted. In the three years which have elapsed since the lectures were delivered a large amount of research has been done, and the author has taken particular care to take into account the work of recent investigators.

The British Journal Photographic Almanac, 1908. London: Henry Greenwood and Co.

The "British Journal Photographic Almanac" is an indispensable guide for the use of the amateur and the professional photographer who will find in it a mass of useful information. An editorial article on the advances made in colour photography during 1907 is not too technical for the amateur, and at the same time the scientific reader will find that it gives a very fair account of the main features of recent work on the subject. Copious notes on improved apparatus and processes give the worker every opportunity of making himself acquainted with novelties, and help him to decide the question of their special value to him, while the lists of formulæ for the principal photographic processes and for the developing of different makes of plates and papers are very full, and have been carefully compiled. The chemical tables give reliable data relating to the principal substances used in photography, and a bibliography contains a classified list of books on different branches of the subject.

Descriptive Biochemie. ("Descriptive Biochemistry"). By Dr. Sigmund Frankel. Wiesbaden: J. F. Bergmann. 1907.

This book gives a very full account of the chemical and physical properties of substances occurring in animal organisms, and of the methods of isolating, synthesising, and quantitatively determining the substances themselves and their degradation products. Although the arrangement of the text is systematic and orderly it is not perhaps the best that could be devised, for there is no connection between the subjects of successive chapters, the substances treated of being classified according to their chemical constitution without regard to their occurrence in the organism, except in one chapter which is given to a very short survey of the organs, secretions, &c. The discussions of certain groups of compounds are out of proportion to their relative importance; for instance, the albuminous substances which are classified according to Hammarsten's system are given special prominence, and nearly thirty pages are devoted to the consideration of albuminous substances containing prostetic groups. As a dictionary of biochemistry the work has much to recommend it, its thoroughness and the full references to literature being excellent features from this point of view. The very rapid advance of physiological chemistry in recent years has made it difficult even for the specialist to keep pace, and the value of a work such as this, which may be relied upon as being up to date and complete, is correspondingly great. A spectral table with which the book is provided gives reproductions of some important absorption spectra. In connection with these it would appear that one of them, No. 4, is incorrectly named, for it bears a greater resemblance to the spectrum of hæmatin in acid solution than to hæmatoporphyrin in alkaline solution, although there is undoubtedly a similarity between the general features of the two spectra.

Cours de Physiologie Moléculaire. ("Course of Molecular Physiology"). By Leo Errera. Edited by H. Schouteden. Bruxelles: Henri Lamertin. 1907.

The point of view and scope of this book are both decidedly novel, and it deals with a branch of science which has as yet been but little systematically studied. The region in which the botanist and the physician should be able to work side by side to their mutual advantage is too often shunned by both, and it is precisely this region with which the author endeavours to help his readers to become acquainted. Physical chemistry is regarded with suspicion by biologists, and the existing text-books on the subject are as a rule too difficult and too full for a botanist to use profitably. Hence the great value of this book, which may be regarded as a treatise on certain aspects of physical chemistry written specially for botanists. The general purpose is excellent, and the method of carrying it out is equally good. The book opens with a discussion of the general properties of matter in the three states of aggregation, and in this section phenomena which are of special importance with reference to the living cell are treated fully; for instance the pages on surface tension are very lucid and explicit. The

mutual penetration of solids and fluids is next discussed, in each section the general considerations being followed by applications to the special case of vegetable tissues. The next chapter treats of the movement of water in the plant, and transpiration, and the book concludes with an unbiassed discussion of the theories which have been put forward to explain the ascension of water to great heights in trees. Each theory is explained and summarised, and the objections to it are carefully stated; finally the author decides in favour of the theory advanced simultaneously by Dixon and Joly and Askenasy, and based upon the cohesion of the column of liquid.

Annuaire pour l'An 1908. ("Annual for the Year 1908"). Paris: Gauthier-Villars.

THIS volume contains besides copious astronomical tables, detailed lists of chemical and physical data, last year's volume having given geographical and statistical information generally. The physical tables include barometric and thermometric correction tables, expansion and vapour tension of liquids, indices of refraction, &c., while in the chemical section thermochemical data, the composition of alloys, &c., are tabulated The book contains in addition articles by G. Bigourdain on the distances of the fixed stars, and by E. Guyon on the School of Practical Astronomy attached to the Observatory at Montsouris.

NOTES AND QUERIES.

**** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

The Mahler Bomb Calorimeter.—A correspondent would like to know the address of the maker of this calorimeter.

MEETINGS FOR THE WEEK

MONDAY, 17th.—Society of Arts, 8. (Cantor Lecture). "Theory and Practice of Clock Making," by H. H. Cunynghame, C.B.

TUESDAY, 18th.—Royal Institution, 3. "Membranes—Their Structure, Uses, and Products," by Prof. William Stirling, M.A., LL.D., D.Sc., &c.

—— Society of Arts, 8. "Banners in Pageantry," by George W. Eve.

WEDNESDAY, 19th.—Society of Arts, 8. "The Law of Treasure Trove," by William Martin, M.A., &c.

—— Microscopical, 8. "Eye-pieces for the Microscope," by E. M. Nelson. "The Life History of a New Protophyte," by E. Tozer. "On Dimorphism in the recent Foraminifer, *Alveolina boscii*," by F. Chapman. Exhibitions of Slides illustrating the Life History of some Diptera, by C. L. Curties, and Improved Mercury Vapour Lamp, by J. E. Barnard.

THURSDAY, 20th.—Royal Institution, 3. "Wood, its Botanical and Technical Aspects," by Prof. William Somerville, M.A., &c.

—— Chemical, 8.30. "Action of Thionyl Chloride and of Phosphorus Pentachloride on the Methylene Ethers of Pyrocatechol Derivatives," by G. Barger. "The Preparation of Conductivity Water," by H. Hartley, N. P. Campbell, and R. H. Poole. "Derivatives of Para-diazoiminobenzene," and "Study of the Diazo-reaction in the Diphenyl Series," by G. T. Morgan and Miss F. M. G. Micklethwait. "Organic Derivatives of Silicon—Part VI., The Optically Active Sulphobenzylethylpropylsilicyl Oxides," by F. S. Kipping. "Simple Manometer for Vacuum Distillation," by N. L. Gebhard.

FRIDAY, 21st.—Royal Institution, 9. "The Ether of Space," by Sir Oliver Lodge.

SATURDAY, 22nd.—Royal Institution, 3. "The Art of Florence," by Selwyn Brinton, M.A.

From GURNEY & JACKSON'S LIST of WORKS on CHEMISTRY.

AN INTRODUCTION to CHEMICAL CRYSTALLOGRAPHY. By P. GROTH, Professor of Mineralogy and Crystallography in the University of Munich. Authorised Translation by HUGH MARSHALL, D.Sc., F.R.S., Lecturer on Chemistry and on Mineralogy and Crystallography in the University of Edinburgh. Crown 8vo. 4s. net.

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Manuals: Alfred Jörgensen, "Micro-organisms and Fermentation" (London and New York, Macmillan & Co., 1900); and "The Practical Management of Pure Yeast" (Loodon, "The Brewing Trade Review," 1903).

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THE CHEMICAL NEWS.

Vol. XCVII., No. 2517.

THE DETECTION OF SODIUM SULPHITE IN THE PRESENCE OF SODIUM SULPHATE AND SODIUM THIOSULPHATE.

By FRANK E. WESTON, B.Sc., F.C.S., and C. W. JEFFREYS.

The usual method for detecting the presence of these three salts when together is not a completely satisfactory one, since the precipitate obtained on adding $BaCl_2$ solution to the aqueous solution of the mixture contains not only $BaSO_4$ and $BaSO_3$, but also BaS_2O_3, the amount of the latter increasing considerably with the concentration of the $Na_2S_2O_3$ in the original solution; hence, on filtering and washing the precipitate, digesting with dilute HCl and filtering, adding Cl water to the filtrate, a white precipitate of $BaSO_4$ may be derived by the oxidation of the sulphurous acid obtained from either the barium sulphite or barium thiosulphate (see Valentin's "Qualitative Analysis").

The authors have arrived at a test by means of which the presence of sodium sulphite can be proved easily in the presence of sodium sulphate and sodium thiosulphate, or in the presence of the sulphates and thiosulphates of the other alkalis.

The principle of the test depends upon:—

a. The insolubility in water of lead sulphate, lead thiosulphate, and lead sulphite.

b. The solubility in a solution of sodium thiosulphate of lead sulphate and lead thiosulphate, and the insolubility in the same of lead sulphite.

The test may be carried out as follows:—To 5 cc. of a solution containing from 0·05 to 0·1 grm. of the mixed salts, add a solution of $Pb(NO_3)_2$ or $Pb(CH_3.COO)_2$ till no further precipitate is produced; a white precipitate* of $PbSO_4$, PbS_2O_3, and $PbSO_3$ is obtained; now add 5 to 6 cc. of a solution of $Na_2S_2O_3$, containing 1 molecular-grm. weight of the crystallised salt per litre of solution, and well shake; filter, and well wash the insoluble $PbSO_3$ on the filter-paper till free from $Na_2S_2O_3$; pour 3 to 4 cc. of dilute H_2SO_4 on the $PbSO_3$, collecting the filtrate in a clean test-tube. SO_2 can be detected in the funnel by smell and sulphurous acid in the filtrate by its decolorising a solution of $KMnO_4$.

In order to test the efficiency of the reaction, the following experiments were performed. Standard solutions of the various salts were made having the following strengths:—

1. Sodium thiosulphate containing Mol./2 $Na_2S_2O_5.5H_2O$, *i.e.*, 124·11 grms. per litre.
2. Sodium thiosulphate containing Mol./20 $Na_2S_2O_5.5H_2O$, *i.e.*, 12·411 grms. per litre.
3. Sodium sulphate containing Mol./20 $Na_2SO_4.10H_2O$, *i.e.*, 16·108 grms. per litre.
4. Sodium sulphite containing Mol./20 $Na_2SO_3.7H_2O$, *i.e.*, 12·608 grms. per litre.
5. Lead nitrate containing Mol./20 $Pb(NO_3)_2$, *i.e.*, 16·549 grms. per litre.

Test Series 1.—Two cc. of Mol./20 solutions were taken and 2 cc. of Mol./20 $Pb(NO_3)_2$ solution added; in each case a thick white precipitate was obtained. Mol./20 $Na_2S_2O_3$ solution was then added till precipitate dissolved, giving a clear solution, and the number of cc. required observed.

(N.B. — It was found by experiment that 2 cc. $Pb(NO_3)_2$ solution was sufficient to precipitate all the sulphate, &c., in each case).

* This precipitate can be washed by allowing to settle, decanting, adding 5 cc. distilled water, shaking, allow to settle, and again decant.

The following average results were obtained:—

i. PbS_2O_3 precipitate required 25 cc. Mol./20 $Na_2S_2O_3$ to dissolve it.

ii. $PbSO_4$ precipitate required 100 cc. Mol./20 $Na_2S_2O_3$ to dissolve it.

iii. $PbSO_3$ precipitate gave with 100 cc. Mol./20 $Na_2S_2O_3$ a thick milky liquid which remained unaltered even with 200 cc. of thio.

Test Series 2.—The insoluble lead salts were formed in precisely the same manner as in Series 1, but were treated with Mol./2 $Na_2S_2O_3$ solution with the following results:—

i. PbS_2O_3 precipitate required 1·2 cc. Mol./2 $Na_2S_2O_3$ to dissolve it.

ii. $PbSO_4$ precipitate required 4·0 cc. Mol./2 $Na_2S_2O_3$ to dissolve it.

iii. $PbSO_3$ precipitate gave with 100 cc. Mol./2 $Na_2S_2O_3$ a thick milky liquid on shaking, and no apparent change even with 200 cc.

Test Series 3.—(A). Two cc. of each of the Solutions 2, 3, and 4 were mixed, and 6 cc. of the $Pb(NO_3)_2$ solution added; a thick white precipitate was obtained, and on filtering the filtrate gave no further precipitate with the $Pb(NO_3)_2$ solution; the precipitate of $PbSO_4$, PbS_2O_3, and $PbSO_3$ was well shaken with 10 cc. of Mol./2 $Na_2S_2O_3$ solution, producing a thick turbid liquid; this was filtered, and the precipitate ($PbSO_3$) well washed with hot water till filtrate gave no reaction for $Na_2S_2O_3$ ($KMnO_4$ and dilute H_2SO_4); 5 cc. of dilute H_2SO_4 were then poured on the filter; SO_2 immediately evolved (smell), and filtrate instantly decolorised a solution of $KMnO_4$.

(B). Two cc. of Na_2SO_4 solution and 2 cc. of the $Na_2S_2O_3$ were mixed, and 4 cc. of $Pb(NO_3)_2$ solution added; a thick white precipitate obtained which dissolved in 4 cc. of Mol./2 $Na_2S_2O_3$ solution; 4 cc. more of the latter solution were added, and to the clear liquid one drop of the Na_2SO_3 solution was added, when a thick precipitate was obtained, insoluble on shaking.

Test Series 4.—In this set of tests Mol. $Na_2S_2O_3$ solution was used for dissolving the $PbSO_4$ and PbS_2O_3, when it was found that 1 to 2 cc. of this solution was sufficient in all cases to completely dissolve these salts formed as in Series 1 to 3.

The authors are further examining the test as to its applicability in the presence of metals forming insoluble sulphites and thiosulphates.

The Polytechnic, Regent Street, W.
February 8, 1908.

EXPERIMENTS ON THE WASTE GASES OF THE CLAUS-CHANCE SULPHUR PROCESS.

By J. C. THOMLINSON, B.Sc.

The following experiments showing that in this process the chemical reactions take place almost entirely in the kilns in which hydrogen sulphide and air pass over iron oxide, and not at all during the passage of the gases through the condensing plant, &c., to the factory chimney, were made with an apparatus of which the following is a sketch.

The bottle A, which contains 10 cc. *n*/10 iodine solution, made up to 250 cc. water and coloured with starch paste, is connected at D with the supply from which the sample is taken by means of an aspirator B, the water of which running into a measure C, gives us the volume of the sample which under working conditions is very nearly those of normal temperature and pressure.

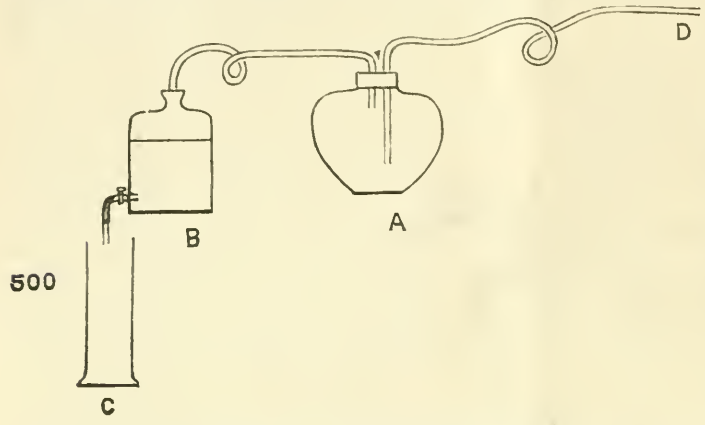
The bottle is shaken thoroughly as soon as the gas is allowed to enter at D until the iodine solution is colourless, when the volume of the sample is read off by the measure C.

This test gives us the total amount of waste sulphur

which is there as sulphuretted hydrogen and sulphur dioxide.

We now titrate against decinormal caustic soda solution, thus getting the sulphur as sulphur dioxide, which in the reaction with the iodine solution is converted into sulphuric acid; the difference between the two results represents sulphur as hydrogen sulphide.

The equation which represents the reaction of sulphur dioxide and hydrogen sulphide on iodine solution will at once show that the decinormal solution is made up with an equivalent of sodium carbonate, which plays an important part in the reaction



$$2Na_2CO_3 + 4I + SO_2 + H_2S = 4NaI + 2CO_2 + S_1 + H_2SO_4.$$

Example.—The volume of gas drawn off is 500 cc., and the volume of decinormal soda solution used to checking the sulphur dioxide in the sample is 5 cc.

10 cc. *n*/10 iodine solution = 0·016 grm. S = 12·5 grains per cubic foot.

5 cc. *n*/10 NaOH solution = 0·008 grm. = 7·0 per cubic foot.

Hence sulphur as H_2S = 5·5 grains per cubic foot.

THE PREPARATION OF FORMAMIDE FROM ETHYL FORMATE AND AMMONIUM HYDROXIDE.

By I. K. PHELPS and C. D. DEMING.

The action of ammonia on an ester is a typical method for the formation of an acid amide. Hofmann (*Ber.*, xv., 977) states that this reaction is particularly easy when the ester itself is somewhat soluble in water; but that in the case of ethyl formate and aqueous ammonia, when allowed to stand at the ordinary temperature, a considerable part of the acid amide is hydrated to ammonium formate, and the amount of acid amide formed is accordingly diminished. He further states that this hydration goes on to such an extent that a yield much in excess of 70 per cent is impossible.

The work given here records the results of experiments which show that such hydration during reaction may be avoided and the formamide may be obtained in amount equal to that indicated by the theory for the action from ethyl formate and ammonia.

Ethyl formate for use in this work was prepared by treating commercial sodium formate with a mixture of absolute alcohol and concentrated sulphuric acid. The crude product obtained as a distillate was fractioned and portions found to boil between 53° and 56° were treated with fused calcium chloride to remove water and alcohol, and re-distilled after filtering from the calcium chloride. This distillate was then treated with dry ammonia gas obtained by boiling concentrated ammonium hydroxide in a flask connected with a return condenser and leading the ammonia gas obtained in this way through a lime tower. The ammonium formate precipitated was separated by filtration, and then, by fractional distillation, pure ethyl formate distilling within two-tenths of a degree was obtained free from ammonia gas or other impurity.

In all the experiments recorded in the table definite weights of the pure ethyl formate, chilled in an ice and salt mixture, were treated with ammonium hydroxide of known strength similarly chilled, and the temperature of the mass was not allowed to rise above 0° until after the reaction between the formate and the ammonia solution had been largely completed. The formamide produced in each case was obtained by separating from impurities by fractioning *in vacuo* in the usual way and distilling the residue after the low-boiling impurities, largely ammonia, ethyl formate, alcohol, and water, had been removed.

In certain experiments the ethyl formate and ammonium hydroxide were mixed in a 250 cc. distilling flask, and the mixture was fractioned *in vacuo* as soon as it had become homogeneous. In this process the 250 cc. distilling flask containing the mixture was connected to a 100 cc. distilling flask used as a receiver, and the formamide was separated from low-boiling impurities by fractioning *in vacuo* in the usual way, the distilling flask being heated in a water-bath at 60° for fifteen minutes after the pressure on the manometer registered 15 mm. The formamide was then distilled over, by heating the distilling flask in a bath of sulphuric acid and potassium sulphate, and caught in the receiver chilled by a current of cold water (see H. Scudder, *Journ. Am. Chem. Soc.*, xxv., 161).

In other experiments the distillation was not made as soon as the ethyl formate and ammonium hydroxide had become homogeneous. In each of these experiments a definite weight of ethyl formate held in a 250 cc. glass-stoppered reagent bottle was treated with pure, commercial ammonium hydroxide of known strength, after chilling each in a mixture of ice and salt, slowly enough so that at no time during mixing did the temperature of the mixture rise above 0°. The mixture at this time consisting of two layers became homogeneous in about five minutes, but was allowed to stand in the ice mixture for fifteen minutes; for the heat given out showed that the reaction progressed after the mass had become homogeneous. This solution was kept tightly stoppered for a definite time, after which it was transferred to a 250 cc. distilling flask connected to a 100 cc. distilling flask used as a receiver, with the use of the least amount of alcohol to remove the last traces from the side-walls of the bottle. The formamide was separated from low-boiling impurities by fractioning *in vacuo* in the manner described, and the formamide distilled and weighed.

It is obvious from the work recorded in the table that three factors are of influence in the quantitative formation of formamide by the interaction in the cold of ethyl formate and ammonium hydroxide,—the excess of the ammonium hydroxide present, the concentration of the ammonia in the solution, and the time during which the interaction of the two is allowed. From Experiments 1 and 2 of section A of the table it is clear that with fixed amounts of ethyl formate and ammonium hydroxide an increase in the length of the time of the reaction is decidedly advantageous. The comparison of Experiments 1 and 2 with Experiments 5 to 12 shows that increasing the amount of ammonium hydroxide gives a yield in excess of that found with the smaller proportion of ammonium hydroxide. A comparison of Experiments 5 to 12 with one another further

emphasises the point that length of time allowed for the completion of the reaction after the mixture has been kept cool during the first of the reaction long enough to prevent hydration is an important factor. It is clear that it is easily possible to obtain the theoretical amount of amide by allowing the mixture to stand five hours or longer. Two hours standing is not quite sufficient.

No.	Ethyl formate.	Ammonium hydroxide (sp. gr. 0·90).	Time of standing.	Formamide. Theory.	Formamide. Found.
	Grms.	Cc.	Hours.	Grms.	Grms.
			A.		
1.	50	30	4½	30·41	19·06
2.	50	30	240	30·41	23·40
3.	50	50	—	30·41	23·57
4.	50	50	—	30·41	22·60
5.	50	50	1	30·41	28·08
6.	50	50	1	30·41	27·40
7.	50	50	2	30·41	29·33
8.	50	50	2	30·41	29·78
9.	50	50	2	30·41	29·80
10.	50	50	5	30·41	30·48
11.	50	50	5	30·41	30·45
12.	50	50	6½	30·41	30·50
			B. *Treatment with* NH_4OH *and Saturation of Mixture with* NH_3.		
13.	50	10	4	30·41	30·45
14.	50	10	4	30·41	30·00
15.	50	20	4	30·41	30·25

In Section B of the table the results shown were obtained by saturating in the cold, at −10° to 0° for about four hours, the ethyl formate and ammonium hydroxide chilled before mixing in a stoppered reagent bottle fitted with a rubber stopper carrying in one perforation a thermometer dipping into the mixture and in the other the delivery tube for the ammonia gas. This mixture on fractioning *in vacuo* as described above and distilling the formamide left in the distilling flask gave the theoretical amount of formamide.

An experiment showed that a definite weight of formamide and water, when fractioned *in vacuo* as in the process outlined, gave an amount of formamide differing from that taken by less than 0·05 grm.

It is evident that it is possible to obtain from ethyl formate by the action of ammonium hydroxide the theoretical amount of formamide. This may be accomplished by treating the chilled ethyl formate with small amounts of chilled ammonium hydroxide and saturating for some hours in the cold with dry ammonia gas; or, more easily, by treating chilled ethyl formate with larger proportions of chilled ammonium hydroxide and allowing the mixture to stand some hours before distilling *in vacuo*. The essential thing in the operation is to keep the mixture of the ethyl formate and the ammonium hydroxide at a temperature so low that ammonium formate is not a product of the action. —*American Journal of Science*, 1907, xxiv., No. 140.

Influence of Addition of Chloride to the Reaction between Barium Carbonate, Carbon, and Nitrogen. —O. Kühling and O. Berkhold.—The results of this investigation prove that additions of more than 2 per cent of barium chloride lower the temperatures at which a mixture of carbonate and carbon absorbs nitrogen. At temperatures at which the mixture absorbs nitrogen without the addition of any other salt barium chloride does not increase the quantity of cyanide formed. The yield of cyanide is either approximately the same, or else is lower when chloride is present. The lowering of the yield of cyanide is specially noticeable when relatively large additions are made. The yield of cyanamide salt seems to be much diminished by the addition of chloride, and it decreases as the quantity of chloride increases.—*Berichte*, xli., No. 1.

THE INFLUENCE OF LIGHT AND OF COPPER ON FERMENTATION.*

By J. E. PURVIS, M.A., St. John's College,
and
W. A. R. WILKS, B.A., Gonville and Caius College.

(Concluded from p. 81).

IV. THE following is the analysis of the unfermented wort :—

Optical activity for 100 per cent solution = +28·6°.

Copper oxide reducing power in 20 cc. of a 20 per cent solution = 1·052 grms. Cu.

The nitrogen content; 25 cc. of N/10 H_2SO_4 were used and 13·5 cc. N/10 NaHO were required to neutralise the excess after Kjeldahling.

The wort was pitched on May 13 at 5 p.m., and the average temperatures between May 14 at 9 a.m. and May 20 at 9 a.m. were :—

Dark .. .. .. = 23·4° C. Red .. .. = 23·4 C.°
White . .. .. = 23·6 Blue .. .. = 23·3

The following gives the results of the analyses of the various fermentations :—

1. Optical activity for 100 per cent solutions at 15° C.

Dark . .. .. = + 5·97° Red .. .. = +4·93
White . .. .. = + 4·60 Blue .. .. = +8·08

2. Copper oxide reducing power in 20 cc. of 20 per cent solutions :—

Dark .. = 0·217 grm. Cu Red .. = 0·159 grm. Cu
White .. = 0·148

3. Specific gravity :—

Dark.. .. .. = 987·80 Red .. .. = 987·38
White .. .. = 987·38

4. The nitrogen content; the numbers represent the cc. of N/10 NaHO required to neutralise excess of acid after the distillation of the NH_3 by the Kjeldahl process :—

Dark .. .. = 17·07 cc. Red .. .. = 17·70 cc.
White .. .. = 17·92

5. The acidity. The following numbers represent the amounts of N/10 alkali used to neutralise 50 cc. of each of the fermentations :—

Dark .. .. = 13·6 cc. Red .. .. = 14·5 cc.
White .. .. = 14·4 Blue .. .. = 31·35

In this IV. series, a small leak was noticed in the cell containing the blue solution, so that a little of the copper sulphate was mixed with the wort. The copper sulphate appeared to inhibit the action of the yeast very greatly, as is seen from the optical activity numbers. The bacteria, however, were not affected to the same extent, for the acidity in the blue instead of being less than in the others was more than twice as great. The increased amount of acid would attack the copper vessel, the development of the yeast would be inhibited to a greater extent than the bacteria, and consequently the acidity would be greatly increased.

But the general results and the effects are comparable with those of the wort II. They were both rich worts.

V. The unfermented wort gave the following analysis :—

Optical activity for 100 per cent solution = +11·43°.

The copper oxide reducing power and the nitrogen content were not determined.

The wort was pitched on May 23 at 4 p.m., and the temperature was 21°. And in addition to the four fermentations in the copper vessels, there was also an additional fermentation in a glass beaker under the influence of white light. The average temperatures between May 23 at 5.30 p.m. and May 28 at 9 a.m. were :—

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* *Proceedings of the Cambridge Philosophical Society*, xiv., Part 4.

Dark	=24·4° C.	Red	=24·7° C.
White	=24·7	Blue.. ..	=24·9
	White (beaker) ..	=24·7	

The following are the results of the analyses of the fermentations :—

1. Optical activity for 100 per cent solutions at 15° C.

Dark	= +5·15°	Red	= +5·00
White	= +5·10	Blue	= +5·13

2. Specific gravity :—

Dark..	=991·43	Red	=991·34
White.	=991·82	Blue	=991·19

3. Acidity. The numbers represent the amounts of N/10 alkali used to neutralise 50 cc. of each fermentation :—

Dark	=20·85 cc.	Red	=13·60 cc.
White	=23·80	Blue	=12·05
	White (in glass beaker) ..	=12·90	

The great diminution in the acidity when the fermentation was carried on in the glass vessel compared with the corresponding experiment in the copper vessel, and under the influence of white light, is noticeable.

B.

In the second series of experiments, the fermentations were carried on in sterilised glass vessels, and the fermenting solutions were not of ordinary hopped wort, but contained :—

Glucose	10·00 per cent.
Ammonium sulphate. ..	0·15 ,,
Ammonium phosphate ..	0·15 ,,

Of this solution 150 cc. were used in I. series of experiments, and the same volume diluted to about one-half the strength in the II. series of experiments. The experiment marked Ia. was conducted in a non-sterilised glass vessel open to the air, and the result showed that the carbon dioxide could easily escape from the other vessels, so that there was nothing to be feared from its action. The other glass vessels were loosely covered with glass-wool, through which thermometers passed into the fermenting wort. The light was filtered through red glass plates for the red rays and through ammoniacal copper solutions for the blue rays, and the effect was compared with the direct effect of white light and with one guarded from contact with any light by the vessel being covered with black cloth. Pure cultures of *S. Cerevisiæ* I. were used to ferment the nutrient solutions.

The optical activity of 100 per cent of the original solutions was = +10·01°. The average temperatures of the series of fermentations between May 28 at 11 a.m. and June 3 at 9 a.m. were :—

I. Dark..	=23·7° C.	II. 23·3° C.	Ia. 22·9° C.
White.	=23·3	23·6	
Red ..	=23·7	23·7	
Blue ..	=23·3	22·9	

After the fermentations the following numbers were obtained for the optical activities :—

I. Dark..	=+2·34° C.	II. +1·85°	Ia. +2·35°
White.	=+2·35	+1·82	
Red ..	=+2·28	+1·81	
Blue ..	=+2·35	+1·81	

C.

In this series of experiments, four were conducted in unsterilised copper vessels, and two in unsterilised copper vessels, using only red and white light for the latter. The optical activity of a 100 per cent solution was about +16°.

The average temperatures between May 30 at 10.30 a.m. and June 3 at 9 a.m. were :—

I. Glass vessels.		II. Copper vessels.	
Dark ..	=21·4° C.	White ..	=22·3° C.
White ..	=22·3	Red	=22·0
Red. ..	=22·3		
Blue ..	=21·3		

The values of the optical activities after the fermentations were :—

I. Glass vessels.		II. Copper vessels.	
Dark..	=+3·42°	White ..	=+4·94°
White.	=+3·48	Red. ..	=+7·61
Red ..	=+3·36		
Blue ..	=+3·43		

The numbers obtained from the fermentations in the glass vessels do not show very great differences, whereas those obtained from the copper vessels are very marked. The great difference between the numbers obtained from the copper vessels compared with those of the glass vessels is also very noticeable.

The values of the acidities after fermentation were the following; the numbers represent the amount of N/10 alkali required to neutralise the acid produced :—

I. Glass vessels.		II. Copper vessels.	
Dark ..	=12·3 cc.	White ..	=57·4 cc.
White ..	=12·5	Red	=81·3
Red. ..	=13·3		
Blue ..	=23·8		

The fermentation in the blue light can hardly be compared with the others because the temperature was very low (only about 19°) for a long time, and this probably affected the vitality of the yeast, so that bacterial action became stronger. The numbers obtained from the copper vessels were also very high, and may be explained by the fact that the wort had remained corked up in a bottle for a day; and although, from the smell, there was no apparent acidification, it is probable there was a development of acid producing bacteria. The acid would dissolve a little of the copper, and thereby retard the action of the yeast.

D.

From a consideration of the results of the fermentations in sections A, B, and C it seemed to be desirable to conduct another series of fermentations in the four copper vessels, in order to discover what amount of copper, if any, was dissolved during the process of the fermentation. And, for this purpose, a litre of hopped wort was placed in each of the vessels, and the fermentations went on for five days under exactly the same conditions as those described in the preceding experiments. At the end of this time, the liquors were filtered, evaporated to dryness, and the residues ignited until all the organic substances were burnt away. What remained was dissolved in acid, and the CuO estimated in the usual way. Owing to an accident, the residue of the fermentation in the red light was lost; but the following numbers show the amounts of CuO obtained from the three others, in percentages of the original wort.

Dark.. ..	=0·0072 per cent CuO
White ..	=0·0051 ,,
Blue.. ..	=0·0052 ,,

There can be little doubt, therefore, that the observed differences in the numbers obtained when the fermentations went on in the copper vessels were due to the solution of a little of the copper influencing the action of the yeast; and it is of interest to note the smaller quantity of CuO found in the fermentations in the white and blue than in the dark.

General Results.

The more important results of the preceding experiments are :—

1. That fermentation when carried on under sterilised and unsterilised conditions in glass vessels, and under the influence of various spectral colours as well as of white light and also in the dark, was not seriously influenced, as shown by determinations of the optical activities of the fermented solutions. The small differences in the numbers and particularly of the acidities may be owing to experimental errors. Further experiments will be necessary to confirm these differences, and with a stronger light, like that of the arc.

2. That fermentation when conducted in copper vessels, but otherwise under the same conditions, is influenced very considerably, as shown by the marked differences in the numbers obtained from the acidity, optical activity, &c. It is not suggested that this influence was caused by rays of light of varying degrees of refrangibility, except indirectly. It appears that copper dissolved from the fermenting vessels largely determined the course of the fermentations. For example, the results obtained under the influence of blue light prove that the inhibitory effect of this light on the development of acidifying bacteria was to decrease the amount of acid produced in the fermenting wort, and, therefore, to lessen the amount of copper dissolved. On the other hand, the fermentations under the influence of red light and in the dark gave better facilities for a more vigorous growth of these bacteria. The acid produced thereby dissolved a little of the copper; and its inhibitory effect on a normal growth of the yeast, and a regular fermentation, is evident from the varying numbers obtained in the different determinations. The larger amount of CuO obtained in the fermentation in the dark as compared with the others appears to be evidence in favour of this view. But contributory causes may be owing to the differences of temperature; for the temperature of the fermentations in the dark and the red were usually a little higher than in the blue, and the solvent action of the acid on the copper would be thereby increased. At the same time it is probable that, as the fermentations proceeded, the CO_2 produced from the break down of the sugar, would also dissolve a little of the copper, and this also should be added as a further influence.

3. Another fact which is indicated by these experiments is the influence of the original composition of the wort. In a good wort, the yeast appeared to resist the action of the copper better than in a poor wort; for the differences in acidity, &c., are much less marked in the good worts than in the poor ones.

In view of these varying results, it will be of importance to study more systematically the influence of different amounts of copper, and of other metals like silver, upon the growth of yeast and fermentation, a problem which has been kindly suggested by Dr. Horace Brown, who called our attention to some experiments conducted at Rothampstead on the influence of small quantities of copper and silver on the growth of various plants.

The above investigation was conducted in the University Chemical Laboratory.

Lecture Experiments with Ozone.—C. Harries.—To demonstrate the absorption of ozone by turpentine-oil a cylinder about 30 cm. high is filled with ozone from the ozoniser, and well shaken with about 50 cc. of oil of turpentine. If a potassium iodide starch-paper is now introduced into the cylinder it remains absolutely unchanged, showing that all the ozone has been absorbed. To show that ozone ignites with oil of turpentine, a high broad cylinder is filled with ozone, and a piece of blotting-paper saturated with turpentine oil, and dried, is quickly put into the cylinder. After a few seconds the turpentine ignites and burns with a dark red luminous flame, much soot being formed.—*Berichte*, xli., No. 1.

THE ELECTROLYTIC DEPOSITION OF ZINC, USING ROTATING ELECTRODES.*

II.

By T. SLATER PRICE, D.Sc.

In a paper read before this Society on June 12, 1906 (*Transactions of the Faraday Society*, 1906, ii., 85; also Chemical News, vol. xciv., p. 18), a special form of apparatus was described for the electrolytic deposition of zinc (and other metals), using a rotating cathode, and also a modification of the apparatus of Kollock and Smith (*Journ. Am. Chem. Soc.*, 1905, xxvii., 1255) was suggested as being more convenient. Since that time the various methods for the deposition of zinc have been more thoroughly tested by the author, and the present communication gives an account of the results obtained.

The experiments were commenced with the idea of investigating the effect on the quantitative deposition of zinc, using a rotating cathode, of the addition of various electrolytes. A solution of zinc sulphate, of approximately known strength, was made up, and in order to determine the amount of zinc present in an aliquot portion the method of Kollock and Smith was used, since the addition of extraneous electrolytes other than sulphuric acid is then unnecessary, and consequently there is less risk of introducing impurities into the solution. The zinc sulphate used was obtained from Kahlbaum; it was re-crystallised, care being taken that crystallisation took place below 39° C. Having found the strength of the solution, experiments were commenced with the rotating cathode. At the outset, however, a difficulty was met with, since the results with the mercury cathode were always lower than the others. It was at first thought that this might be due to some of the zinc being deposited in the spongy condition when the platinum cathode was used, but further experiments did nor support this view. The method of Kollock and Smith was therefore subjected to a closer examination.

Since electrolytic methods for the quantitative estimation of zinc were in question, it was necessary to analyse the zinc sulphate used by the ordinary methods of quantitative analysis. The most convenient method of doing this, and one which avoids any loss due to manipulation, is to heat the salt in a platinum crucible, and convert it directly into the oxide (*cf.* Fresenius, "Quant. Analysis"). The heating was done very carefully at first, and after all the water of crystallisation had been driven off, the crucible was gradually raised to a high temperature by means of a Mecker burner, and heated till the weight was constant. In same cases the zinc sulphate was weighed directly into the crucible, and in others 10 cc. of a solution containing a known weight of the salt were pipetted into the crucible, and evaporated to dryness on the water-bath. The mean percentage of zinc obtained from seven determinations was 22·74, the greatest deviation from the mean being 0·03. The calculated percentage of zinc in $ZnSO_4.7H_2O$ is 22·74, so that the zinc sulphate used may be taken as pure.

For each electrolytic determination 1 grm. of zinc sulphate, contained in 10 cc. of a solution of the salt, was taken. In some few cases 1 grm. of the sulphate was weighed out directly and used for the determination, this making no difference in the results obtained. All the weights, pipettes, &c., used had been carefully calibrated.

Experiments Using the Rotating Cathode.

In the experiments described in the previous paper the platinum cathode was always silvered before being used, but since Medway (*Amer. Journ. Sci.*, 1904, iv., 18, 56), using a platinum crucible for the rotating cathode, found that it was unnecessary to first coat it with either silver or copper, a number of determinations were made without previous treatment of the cathode. It was found that if the zinc was dissolved off soon after it had been deposited

* A Paper read before the Faraday Society, March 19, 1907.

Table I.

Grms. of Na_2SO_4.	Grms. of Na acetate.	Drops of glacial acetic acid (*a*).	Cc. of 0·880 NH_4OH.	C.	V.	*t*.	Per cent Zn.	Error.
2	1	—	—	2	5·5—6·5	15	22·84	+0·10 (*b*)
2	1	—	—	2	6—7	14	22·82	−0·08 (*c*)
2	1	2	—	2	—	18	22·82	+0·08 (*c*)
2	1	2	—	2	—	14	22·79	+0·05 (*b*)
2	1	3	—	2	6·5	19	22·86	+0·12 (*b*)
3	1	3	—	2	—	14	22·84	+0·10 (*b*)
2	1 [1]	—	—	0·35 (2), 2 (13)	—	15	22·84	+0·10 (*b*)
2	1+1 [8]	2	—	2	—	13	22·85	+0·10 (*b*)
—	2 [19]	—	—	0·25 (7), 0·5 (3), 1 (9), 2 (10)	—	29	22·76	+0·02 (*b*)
2	1	3	0·5 [14]	0·5 (4), 1 (5), 2 (10)	—	19	22·84	+0·10 (*c*)
2	1	6	1 [15]	2	—	20	22·81	+0·07 (*c*)

(*a*) 40 drops = 1 cc. (*b*) Trace. (*c*) All out.

Table II.

Grms. of Na_2SO_4.	Grms. of Na acetate.	Drops of glacial acetic acid.	C.	V.	*t*.	Per cent Zn.	Error.
2	1	2	2	6·5	14	22·74	0·00
2	1	2	0·5 (8), 1 (30), 2 (5)	—	43	22·71	−0·03
2	1	2	2	—	14	22·71	−0·03
2	1	—	2	6	15	22·75	+0·01
2	1	—	2	—	15	22·73	−0·01
2	1	—	2	6·5	13	22·72	−0·02
2	1	—	2	—	14	22·79	+0·05
2 (*a*)	1	—	2	—	14	22·71	−0·03

(*a*) In this case the electrode was coated with copper instead of with silver.

the cathode was not affected, but if the deposit was allowed to remain on the platinum for some time it gradually alloyed with it, as is the case when the ordinary method, using a stationary cathode (and anode), is used.

The results obtained are given in Table I., where C is the current used, V is the voltage, and *t* the time of deposition (in minutes). The voltage was not measured in every case. In those cases where the current was gradually increased the numbers in round brackets represent the time (in minutes) during which the current was kept at the value given by the figures before the bracket. The numbers in square brackets denote the number of minutes the electrolysis had been proceeding before the reagent in question was added. The notes denote whether the deposition was complete, or whether a trace of zinc remained in solution. The cathode used had the dimensions given in the previous paper, and the number of revolutions per minute was 600—700. The electrolytes added were sodium sulphate and acetate, since the previous investigation showed that good results were then obtained.

The results are high in every case, so that there is evidently a systematic error. Moreover, in spite of the high results, in most cases a trace of zinc was left in solution. Potassium ferrocyanide was used in testing for zinc, 5 cc. of the solution from which the zinc had been deposited being taken for the test. The test is very delicate, and rough quantitative measurements gave that the amount of zinc left in the solution, as indicated by the term "trace," was from 0·0002 to 0·0006 grm.; if this amount of zinc were allowed for, the percentages of zinc found would be slightly higher than those given.

It is possible that the high result is due to the deposition of a small amount of spongy zinc. The deposition potential of the hydrogen ions on platinum is less than that of the zinc ions, and consequently the former would be deposited in preference to the latter. In spite of the vigorous stirring of the electrolyte it is possible that an excess of hydroxyl (OH) ions would be left in the solution in the neighbourhood of the cathode at the commencement of the electrolysis, with the consequent formation of zinc hydroxide and deposition of spongy zinc (*cf.*, Foerster, "Elektrochemie wässeriger Lösungen," p. 290).

Experiments in which acetic acid was added, or the current gradually increased, gave no better results. In some cases the error was very small, and it was hoped that a good method had been found, but repetition, under what seemed to be the same conditions, gave a bad result; sometimes a series of good results would be obtained, and these would be followed by a series of bad ones (the table does not give the results of all the experiments carried out; those omitted lie between the extreme results given). This is only a particular case of what occasionally occurs in zinc depositions, viz., that certain methods often give good results at first, but further trial shows them to be unsatisfactory.

When ammonia was added all the zinc was deposited, but the results were uniformly high.

The position of the cathode with respect to the anode has an effect on the deposit. If it is placed so that the bottom edge is about level with the lower ring of the anode, the deposit on the lower part is liable to be spongy; the concentration of the stream lines of the current would be greater on this lower part, thus increasing the current density too much. To obviate this the cathode was placed (approximately) in a symmetrical position with respect to the anode ring.

To do away with any error which might be due to impurities in the sodium sulphate and acetate, these salts were re-crystallised; but the results were no better.

The results apparently were independent of the manner in which the cathode was treated, as was shown by a number of experiments.

In all the following experiments, except where specially stated, the electrode was silvered before the zinc was deposited on it. It was found most convenient to dissolve off both the zinc and the silver after each estimation, and not to endeavour to use the same coating of silver throughout all the experiments (*cf.*, Ingham, *Journ. Am. Chem. Soc.*, 1904, xxvi., 1269). The saving in time thus effected, using a rotating cathode for the silvering, compensates for the increased amount of silver used.

The first series of experiments gives some of the results obtained when sodium sulphate and acetate, with or without the addition of acetic acid, are used (see Table II.).

(To be continued).

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

Ordinary Meeting, February 6th, 1908.

Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

The President referred to the loss sustained by the Society owing to the death of Mr. W. A. Shenstone, F.R.S. (elected in 1876), and of Mr. R. J. Friswell (elected in 1871).

Certificates were read for the first time in favour of Messrs. Arthur John Allmand, B.Sc., Central Laboratories, Widnes; William Henry Benson Baker, B.A., Frognal Dene, Hampstead, N.W.; Josiah Leonard Bowen, 8, West Field, Lightcliffe, near Halifax; Charles Gilling, 30, Carnarvon Road, Barnet; Alwyne Harcourt Meade, Cedar House, St. Neots; Herbert Richard Neech, 20, Colegrave Street, Lincoln; Thomas Richards Phillips, Stanhope House, Abergavenny; Francis Edward Richards, B.Sc., County Secondary School, Redruth; William Wheatley, B.A., 21, Bairstow Street, Preston.

A ballot for the election of Honorary and Foreign Members was held, and the following were subsequently declared duly elected:—Armand Emile Justin Gautier, Albin Haller, Johann Wilhelm Hittorf, Joseph Achille Le Bel, Henry Louis Le Chatelier, Theodore William Richards, Otto Wallach.

Of the following papers, those marked * were read:—

*14. "*The Metallic Picrates.*" By Oswald Silberrad and Henry Ablett Phillips.

Older investigations on the picrates show so many discrepancies that a systematic revision of the work has been undertaken, with the result that the water of crystallisation and properties of the commoner salts have been definitely established. Several new salts were also described.

*15. "*Some Physico-chemical Properties of Mixtures of Pyridine and Water.*" By Harold Hartley, Noel Garrod Thomas, and Malcolm Percival Applebey.

With the view of examining the effect of the gradual replacement of water by pyridine on the electrical conductivity of salt solutions, and of tracing a connection between the properties of the solvent and of the solution, the following physical constants have been determined:—The density, viscosity, and surface tension of pyridine-water mixtures at 0° and 25°, the density and viscosity of one-eighth weight-normal solutions of lithium nitrate in a series of mixtures at 0° and 25°, and the molecular conductivity of these solutions at various dilutions at the same temperatures.

The density and viscosity curves all show a maximum deviation from the line joining the end values in the neighbourhood of 30 mol. per cent pyridine, both at 0° and 25°. No evidence was found for the existence of the discontinuities described by Dunstan, Thole, and Hunt (*Trans.*, 1907, xci., 1718) all the observations lying on smooth curves.

By the application of Stokes's equation respecting the limiting velocity of a small sphere moving in a viscous medium under the influence of a constant force, the variation in the size of the solvent atmospheres attached to the ions at infinite dilution has been calculated.

It was shown to what extent the variations of the molecular conductivity of lithium nitrate solutions with the composition of the solvent can be ascribed to changes—(1) in the coefficient of ionisation, (2) in the fluidity of the solution, and (3) in the aggregation of solvent particles round the ions.

Discussion.

Mr. Dunstan pointed out that some misconception had evidently arisen in the minds of the authors as to the curves published by Messrs. Thole, Hunt, and himself (*Trans.*, 1907, xci., 1728). For the purpose of more clearly representing the composition of the hydrates of pyridine, the tangents to the curves at the points of flexure were produced, and this gave rise to the erroneous impression that the curves were built up in sections. He also drew attention to the fact that every such "discontinuity" in the density curve was repeated in the viscosity curve, and instanced the work of Pickering in support of the contention that such hydrates do exist in solution.

Mr. R. J. Caldwell agreed with the authors that the usefulness of most previous work on strong solutions is impaired by the fact that "volume normal" solutions have been employed instead of solutions made up by weight. He had already measured electrical conductivities of solutions made up by weight, taking account of the density, as the authors appeared to have done.

The specific rotatory power of sucrose varied from 66·5° in pure water to 83·8° in pure pyridine, but until the concentration of the pyridine reached 30 per cent the rotatory power did not vary much from the value obtained in pure water (Wilcox, *Journ. Physical Chem.*, 1901, v., 592). At low concentrations, the pyridine, existing doubtless in a hydrated condition, was prevented from exerting any influence on the dissolved sugar. The values obtained by the authors for the conductivity of lithium nitrate appeared to be entirely analogous, leading to the same conclusion with regard to the pyridine.

Mr. Hartley said that he did not believe in the existence of any irregularities in the density or viscosity curves, as the greater the care with which the determinations were made the more nearly did the experimental values lie on smooth curves. The determination of density was so much more accurate an operation than the determination of viscosity, that he did not think the anomalies in the viscosity curves could be explained by those in the density curves. In reply to Dr. Barger, he said that the authors recognised that pyridine possessed residual valencies, although the liquid molecules were probably unassociated, otherwise it would have no dissociating influence on salts dissolved in it.

*16. "*The Constitution of Umbellulone.* (Part III.). By Frank Tutin.

Semmler's recent statements (*Ber.*, 1907, xl., 5017) respecting the constitution of umbellulone are based on experiments conducted with "β-dihydroumbellulone" and its derivatives. Since the material employed by Semmler consisted of highly impure umbellulone, there is no evidence in support of the assumption that "β-dihydroumbellulone" is a derivative of umbellulone, but, on the other hand, the experimental facts lead to the contrary conclusion.

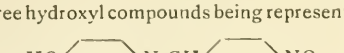
In addition to this uncertainty regarding the source of the preparation which had been called "β-dihydroumbellulone," this has now been shown to be a mixture, consisting chiefly of an unsaturated ketone, but also containing a saturated one, and it can only be from the latter that Semmler has prepared homotanacetonedicarboxylic acid.

Semmler's results, therefore, are devoid of significance in so far as they pertain to the constitution of umbellulone.

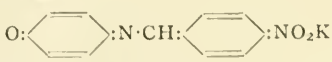
*17. "*Colour and Constitution of Azomethine Compounds.*" (Part I.). By Frank George Pope.

The nitrohydroxyazomethine compounds show an entirely different absorption spectrum from that of their alkali salts when the nitro- and hydroxyl-groups are in the para-position to the azomethine group, and, from the similarity of the ·N:CH· grouping to the ·N:N· grouping in many respects, it would seem apparent that the alkali salts of these compounds could be formulated on a di-quinonoid

basis, the free hydroxyl compounds being represented thus:—



and the alkali salts as—



(compare Hewitt and Mitchell, *Trans.*, 1907, xci., 1251).

A similar state of things may also be observed, although to a slightly less extent as regards absorption, when the nitro- and hydroxyl-groups are in the ortho- and para-positions to the azomethine grouping.

The following compounds were described:—p-4-*Nitrobenzylideneaminophenol*, m. p. 168·5°; o-4-*nitrobenzylideneaminophenol*, m. p. 161°; p-3-*nitrobenzylideneaminophenol*, m. p. 154°; o-3-*nitrobenzylideneaminophenol*, m. p. 135°; o-*hydroxybenzylidene*-m-*nitroaniline*, m. p. 132°.

Discussion.

Dr. Hewitt remarked that, whilst the general type of absorption was similar for corresponding azo- and azomethine compounds, replacement of a nitrogen atom by a methenyl group increased the oscillation frequency.

*18. "*The Preparation of l-Benzoin.*" By Alexander McKenzie and Henry Wren.

l-Benzoin, obtained from *l*-mandelamide and magnesium phenyl bromide, melts at 131—132·5°, reduces Fehling's solution, and has $[\alpha]_D$ 105 − 118·6° for $c = 0·9232$ in acetone solution.

Discussion.

Dr. McKenzie, in reply to Dr. Lowry and Dr. Lander, stated that no racemisation, either partial or complete, had so far been observed with *l*-benzoin.

19. "*Organic Derivatives of Silicon.* Part V. *Benzylethylsilicone, Dibenzylsilicone, and other Benzyl and Benzylethyl Derivatives of Silicane.*" By Robert Robison and Frederic Stanley Kipping.

Benzylethylsilicone, BzEtSiO, prepared from benzylethylsilicon dichloride (Kipping, *Trans.*, 1907, xci., 720), has little in common with benzyl ethyl ketone; it boils at 305—315° (22 mm.), is not reduced by various reagents, and gives neither an oxime nor a hydrazone; molecular weight determinations in acetic acid solution point to the formula $(BzEtSiO)_3$.

Benzylethylsiliconesulphonic acid is easily obtained by sulphonating the silicone with sulphuric acid; the *barium* salt, $(C_9H_{11}SiSO_4)_2Ba$, is soluble in water, but does not crystallise well.

Dibenzyl ethyl silicol, $Bz_2EtSi{\cdot}OH$, was obtained as an oil; it passes spontaneously into *dibenzylethylsilicyl oxide*, $(BzEtSi)_2O$, a crystalline substance melting at 54°.

Tribenzylsilicyl chloride, Bz_3SiCl, crystallises in prisms melting at 141°, and is decomposed by water, giving tribenzylsilicol.

Dibenzylsilicon dichloride, Bz_2SiCl_2, prepared from silicon tetrachloride and magnesium benzyl chloride, crystallises in massive prisms, and melts at 50—52°; when decomposed with water, it yields a *hydrol* of the molecular formula $Bz_2Si(OH)_2$, which crystallises in long asbestos-like needles melting at about 101° (*α-hydrol*), and also an isomeric *hydrol*, which forms large, transparent prisms melting at about 75° (*β-hydrol*); the latter was recently described by Dilthey (*Ber.*, 1905, xxxviii., 4132). In some cases, only one of these hydrols is formed, and in others both are obtained, the *β*-isomeride predominating, but the conditions which determine their formation are unknown. Both hydrols pass into *dibenzylsilicone* (an oil) when they are heated, and the *β*-compound is readily reproduced by treating this oil with water; the *α*-hydrol is not regenerated in this way. Both hydrols give termolecular *dibenzylsilicone*, $(Bz_2SiO)_3$ (m. p. 98°), when they are heated with acetic anhydride.

The experimental data do not yet afford any explanation of the existence and relationship of these isomeric hydrols.

20. "*The Residual Affinity of the Coumarins and Thiocoumarins as shown by their Additive Compounds.*" By Arthur Clayton.

The coumarins and thiocoumarins combine with mercuric chloride, forming compounds of the type $R,HgCl_2$, where R is a coumarin or a thiocoumarin. This combination takes place with the following coumarins and their sulphur analogues:—Coumarin, 7-methylcoumarin, 4:7-dimethylcoumarin; 3:4:7-trimethylcoumarin, thiocoumarin, 7-*methylcoumarin* m. p. 125—126°, 4:7-*dimethylthiocoumarin* m. p. 118—119°; and 3:4:7-*trimethylthiocoumarin* m. p. 124—125°. The thiocoumarins are prepared by the action of phosphorus pentasulphide on the corresponding coumarins, and unlike the coumarins, yields oximes and phenylhydrazones.

Other oxonium compounds of the coumarins were described.

21. "*The Influence of Foreign Substances on Certain Transition Temperatures and the Determination of Molecular Weights.*" By Harry Medforth Dawson and Colin Gyrth Jackson.

The depression of the temperatures at which changes take place in certain condensed systems on the addition of foreign substances has been examined. The changes investigated were:—(1) The conversion of sodium thiosulphate primary pentahydrate into the corresponding dihydrate at 48·1°; (2) the transformation of sodium bromide dihydrate into the anhydrous salt at 50·67°; and (3) the formation of tachhydrite $(CaCl_2,2MgCl_2,12H_2O)$ from calcium and magnesium chloride hexahydrates at 22·40°.

Constants representing the depression of the transition temperature when 1 grm.-molecule of the foreign substance is contained in 100 grms. of the saturated transition solution have been calculated. From a knowledge of these constants, the corresponding invariant points may be utilised for the purpose of obtaining the molecular weights of dissolved substances.

22. "*The Bromination of* p-*Hydroxydiphenylamine.*" By Alice Emily Smith and Kennedy Joseph Previté Orton.

The bromination of *p*-hydroxydiphenylamine is rendered difficult by the readiness with which oxidation to a quinoneanil, $Ar{\cdot}N{:}C_6H_4{:}O$, is effected. All attempts to prepare mono- or di-bromo-derivatives failed, a tribromo-compound apparently being the primary product of bromination. It is a very remarkable fact that isomeric tri- and tetra-bromo-derivatives are not formed, the successive entrance of the bromine atoms following a single definite course.

The *tri-*, *tetra-*, *penta-*, *hepta-*, and *octa-bromo*-p *hydroxydiphenylamines*, and the corresponding *benzoxy*-derivatives and *quinoneanils* (*phenyliminoquinones*) were described.

23 "*The Decomposition of Ammonium Dichromate by Heat.*" By William Marrs Hooton.

It is generally stated that ammonium dichromate on ignition decomposes quantitatively into nitrogen, water, and chromium sesquoxide; but Darby, in 1849, pointed out that a little ammonia was always liberated, and the author has found that the gaseous products of decomposition in air or in a vacuum always contain appreciable amounts of oxygen and oxides of nitrogen. Moreover, the solid residue is not homogeneous: it contains dark brown flakes, and evolves water when heated to bright redness.

If, instead of igniting the salt, it is decomposed slowly by heating it in air below its ignition temperature (190°) until the weight is constant, atmospheric oxygen takes part in the change. The final product is a hydrated form of chromium dioxide, having the composition $2CrO_2,H_2O$. It is a glistening black powder, which on being strongly heated yields oxygen, water, and chromium sesquioxide without incandescence. When heated with hydrochloric acid, chlorine is freely evolved. When boiled with potassium hydroxide solution, it yields potassium chromate and chromium hydroxide.

If ammonium dichromate is heated below its ignition temperature in a vacuum or in absence of oxygen, the final product is a dull greenish black powder having the composition $H_2Cr_2O_4$. This is not a hydrated form of chromium sesquioxide, for it incandesces brightly when heated to 400°. Even after boiling with water, filtering, and drying, it still incandesces when heated to 400°. During incandescence, water is formed, but no gas is liberated, and the sesquioxide formed is not bulky. This compound is not acted on by boiling potassium hydroxide solution, and only slowly by hot hydrochloric acid, no chlorine being evolved.

24. "*The Effect of Constitution on the Rotatory Power of Optically Active Nitrogen Compounds.*" (Part II.). By Humphrey Owen Jones and John Robertshaw Hill.

The authors have resolved a set of five optically active nitrogen compounds, and have determined the rotatory powers of the basic ions (compare *Trans.*, 1906, lxxxix., 282).

The compounds contain the *p*-bromophenyl, methyl, and allyl groups with one of the homologous groups, ethyl, *n*- or *iso*propyl, *iso*butyl, or *iso*amyl, and differ from those, forming one of the sets already described only in the replacement of one of the hydrogen atoms of the phenyl group by bromine.

The *n*-propyl, *iso*butyl, and *iso*amyl compounds were resolved by means of *d*-bromocamphorsulphonic acid, the *iso*propyl compound by means of *d*-camphorsulphonic acid, and the ethyl compound by means of *d*-tartaric acid. The following table summarises the results obtained :—

	Melting point of iodide.	Molecular rotatory power— Of ion at 15°.	Of iodide in alcohol.
Ethyl.. ..	142—143°	−31°(?)	−20°
n-Propyl ..	142—143	+141	+144
*iso*Propyl ..	153	+161	+165
*iso*Butyl ..	133—134	+96	+117
*iso*Amyl ..	135—136	+94	+111

The rotatory power of the iodide in chloroform was determined when possible, and was found to be greater than in alcohol; autoracemisation of the iodide occurred in chloroform in all cases.

The maximum rotatory power is found in the propyl compounds just as in the set of unbrominated compounds, also the rotatory power of this set of compounds, with the exception of the ethyl compound, is considerably greater than that of the unbrominated set.

25. "*Malacone, a Silicate of Zirconium.*" By Alexander Charles Cumming.

The author finds that the formula ZrO_2,SiO_2 corresponds more closely with the observed composition of malacone than does the formula $3ZrO_2,2SiO_2$ assigned to it by Kitchin and Winterson (*Trans.*, 1906, lxxxix., 1568).

A detailed examination gave no reason to suspect the identity of the zirconia, or to suspect the presence of an unknown impurity. The presence of argon cannot be explained by the presence of any new radio-active element, as the radio-activity can be sufficiently accounted for by the presence of radium.

26. "*The Reducibility of Magnesium Oxide by Carbon.*" By Roland Edgar Slade.

The isolation of magnesium by direct reduction of the oxide by carbon has been effected at temperatures above 1700°, and the chief hindrance to the preparation of the metal by this reaction has been found to be due to the back reaction which occurs at lower temperatures between magnesium and carbon monoxide.

Various methods were adopted for removing the metal from contact with the carbon monoxide. Rapid evacuation of the vessel in which the reaction occurs, absorption of the magnesium by molten copper, and reduction of magnesia in presence of aluminium, or in a swift stream of hydrogen, have all proved successful.

27. "*The Crystal Form of Halogen Derivatives of Open-chain Hydrocarbons with reference to the Barlow-Pope Theory of Structure.*" By Frans Maurits Jaeger.

The author has determined the crystalline forms of a number of halogen derivatives of open-chain hydrocarbons, such as tetrabromo-$\beta\beta$-dimethylpropane, 1 : 3 : 5-hexatriene, di- and tetra-bromide and tetra-iodoethylene, for the purpose of ascertaining whether predictions concerning their crystalline form, based on the theory of Barlow and Pope, are justified by the experimental results. In accordance with the indications of the theory, it is found that the substances named above exhibit a close morphotropic relationship. The theory also allows of the prediction that tetrabromo-$\beta\beta$-dimethylpropane should be represented by a pseudo-cubic assemblage; actually it is found that, although the compound crystallises in the monosymmetric system, it is pseudo-cubic.

28. "*The Determination of the Rate of Chemical Change by Measurement of the Gases Evolved.*" By Francis Edward Everard Lamplough.

Further work on the above subject has confirmed the results given in a former communication (*Proc.*, 1906, xxii., 280), with the exception of the paragraph referring to the decomposition of ammonium nitrite.

A few experiments have been performed on the action of sodium hypochlorite on carbamide. The rate of evolution of gas does not give results which can be interpreted by a simple law, owing to the complexity of the reaction; the velocity of the reaction, as measured by the rate of evolution of gas, rises to a maximum and then diminishes.

The reaction between nickel carbonyl and iodine has been found to be of a complex nature, even in cases where either reagent is in considerable excess. When the nickel carbonyl is present in great excess, a remarkable phenomenon is met with, the action proceeding in a steady manner until a point is reached at which it abruptly terminates without warning.

29. "*The Temperatures of Spontaneous Crystallisation of Mixed Solutions, and their Determination by Means of the Index of Refraction. Mixtures of Solutions of Sodium Nitrate and Lead Nitrate.*" By Florence Isaac.

Previous experiments on simple solutions established a "super-solubility curve" which marks their temperatures of "spontaneous" crystallisation.

The supersolubility curve for a mixture of three constituents, sodium nitrate, lead nitrate, and water, has now been determined by measurement of the refractive indices.

In the first set of twenty-two experiments, the proportion of lead nitrate to water was kept constant as 3 : 10, whilst the amount of sodium nitrate varied; in the second set of seventeen experiments, the proportion of sodium nitrate to water was kept constant as 3 : 4, whilst the amount of lead nitrate varied.

In both cases it was found that as the temperature of the liquid falls the refractive index rises to a maximum value. A few crystals usually appear in the supersaturated solution before the maximum index is reached, and at, or about, the maximum point spontaneous crystallisation sets in and gives rise to a dense shower of crystals.

In each set, these maximum points determine the "supersolubility" curve.

The two supersolubility curves may be regarded as plane sections of a supersolubility surface for all possible mixtures of the three constituents.

The curves of spontaneous crystallisation were also determined by experiments with the same solutions in sealed glass tubes. These cannot be made to crystallise until they have reached the temperature already determined from the refractive indices.

The solubility curves for these mixtures were also determined, and their relation to the supersolubility curves established.

30. "*Contributions to the Chemistry of the Terpenes.* Part III. *Some Oxidation Products of Pinene.*" By

George Gerald Henderson and Isidore Morris Heilbron.

The acid $C_9H_{15}CO_2H$, obtained from pinene as previously described (Henderson and Gray, *Trans.*, 1903, lxxxiii., 1299), could not be brominated directly, but was converted into its *chloride*, a viscous, colourless oil. When heated with bromine, this yields the *chloride* of a *bromo-acid*, $C_9H_{14}Br{\cdot}COCl$, an oily liquid, from which, with water, the *bromo-acid*, $C_9H_{14}Br{\cdot}CO_2H$, was obtained. This is a crystalline solid, and when boiled with aqueous sodium carbonate yields the *hydroxy-acid*, $C_9H_{14}(OH).CO_2H$, crystallising from water in colourless prisms. Its *sodium* salt is readily, and its *silver* salt very sparingly, soluble in water.

In preparing the bromo-acid, a small quantity of a crystalline, neutral *compound*, apparently of the composition $C_{10}H_{13}OBr$, separated. Along with the hydroxy-acid there was also obtained a small amount of another *acid*, probably of the formula $C_{10}H_{14}O_2$, which is crystalline and insoluble in water. Its *silver* salt crystallises from water in colourless needles.

The ketone previously described (*loc. cit.*) has now been obtained in a pure state, and has the formula $C_9H_{14}O$. On reduction, it yields the *alcohol*, $C_9H_{15}{\cdot}OH$, a colourless, oily liquid, from which a *phenylurethane* and an *acid phthalic ester*, both crystalline solids, have been prepared.

When heated with ammonium formate, the ketone is converted into the formyl derivative of an *amine*, $C_9H_{15}{\cdot}NH_2$, which is a colourless liquid with a disagreeable odour, and is almost insoluble in water. Its *hydrochloride*, which is extremely easily soluble in water, crystallises in silky needles, and its *platinichloride* in pale yellow leaflets.

The chlorinated oxidation product which is separated during the purification of the ketone is a white, crystalline solid of formula $C_{10}H_{15}OCl$. It is slowly decomposed when heated with alcoholic sodium ethoxide, and yields a colourless, crystalline compound, which does not contain chlorine and has a penetrating odour.

31. "*A β-lactonic Acid from Acetone and Malonic Acid.*" By Andrew Norman Meldrum.

When malonic acid and acetone are mixed with acetic anhydride and a little sulphuric acid, the malonic acid dissolves, and after twenty-four hours a new, crystalline acid is obtained, which melts at 97° and decomposes at a higher temperature. The composition and the molecular weight (determined by the boiling-point method) lead to the formula $C_6H_8O_4$.

The substance is saturated; it decomposes easily, under various conditions, into acetone and malonic acid (or, in place of malonic acid, carbon dioxide, and acetic acid), and when heated with aniline it gives, acetone, carbon dioxide, and acetanilide.

Since the acid is monobasic and yields the salts $C_6H_7O_4Ag$, $C_6H_7O_4Na$, $C_6H_7O_4K,H_2O$, it is evidently the *β-lactone* of *β-hydroxyisopropylmalonic acid*,—

$$\begin{array}{l} CMe_2{\cdot}CH{\cdot}CO_2H. \\ \quad|\quad\quad| \\ \quad O\text{——}C \end{array}$$

PHYSICAL SOCIETY.

A Dinner of the Society was held on Tuesday, February 11th, at the Hotel Cecil, London, when the chair was taken by the President, Prof. J. Perry, F.R.S., and a number of distinguished guests and Fellows of the Society were present, including Sir David Gill, K.C.B., F.R.S.; Sir William Ramsay, K.C.B., F.R.S.; Sir William White, K.C.B., F.R.S.; Sir J. Denison Pender, K.C.M.G.; Rear-Admiral Sir H. B. Jackson, K.C.V.O.; Principal Sir Arthur Rücker, F.R.S.; Sir Joseph Swan, F.R.S.; Col. R. E. Crompton, C.B., R.E.; Prof. W. G. Adams, F.R.S.; Mr. Shelford Bidwell, F.R.S.; Dr. C. Chree, F.R.S.; Mr. W. Duddell, F.R.S.; Prof. Carey Foster, F.R.S.; Dr. R. T. Glazebrook, F.R.S.; Prof. Reinold, F.R.S.; Mr. J. Swinburne, F.R.S.; Prof. S. P. Thompson, F.R.S.; and Dr. W. Watson, F.R.S.

Sir Arthur Rücker, in proposing the toast of "Our Guests," remarked that it was perhaps a little difficult to understand why all the guests that evening were not already Fellows of the Society; if they were not, they certainly ought to be, for the work of such men as Sir David Gill (whom we welcomed back to this country, though the loss to South Africa was great) and of Sir William White was intimately connected with the objects of the Physical Society.

Sir David Gill, in responding, expressed his pleasure at being present as a guest of the Society, and referred to the foremost position hitherto occupied by Great Britain in the world of physics, as shown by the honoured names of Faraday, Maxwell, Kelvin, and others, whose traditions were now being handed down by such men as Lord Rayleigh and Prof. J. J. Thomson.

Sir William Ramsay, in responding to the same toast, dwelt on the relations of physics and chemistry. A great deal of useless physical work was done at times because the physicist determined the physical constants of substances without troubling to ensure the purity of the body under observation. This remark applied, for example, to a great deal of Regnault's work. Chemistry had been defined by Huxley as the dirty part of physics. However true that definition might have been at the time when it was given, chemistry had now outgrown such a statement, and had extended its field not merely into close touch with physics, but with mathematics also. In fact one of the chief difficulties of the chemist at the present time was the solution of the mathematical problems involved in chemistry, and there would be a great opening for "tame mathematicians" who would hold themselves at the disposal of the chemist.

In response to the President, Prof. E. B. Rosa, of the National Bureau of Standards, Washington, expressed his pleasure at being able to be present on this occasion. He had been much interested in visiting the National Physical Laboratory, and observing the great progress that had been made since his last visit five years ago. At the National Bureau of Standards they were making satisfactory headway, and he hoped that the laboratory would shortly be equal to any national laboratory in the world. In the United States they were spending a great deal of money on the science of agriculture, because agriculture was a national asset. He suggested that England similarly might find it a profitable investment to devote the money spent in constructing one battleship per annum to the National Physical Laboratory, instead of preparing for war.

Sir William White, in proposing the toast of "The Physical Society," congratulated the Society on accomplishing so much in a comparatively short life. Unfortunately it became more and more necessary to specialise. Physics was the basis of many of our societies; but, however comprehensive a society might be, new societies sprang up from time to time, and individually we had to be content with a small corner of knowledge.

In responding, The President dwelt on the importance of research. At the present day there were many science teachers and many compilers of books who did no research. They were well up in the letter of science, but not in the spirit thereof, with the result that their writings lacked a most essential quality which could be gained only by actual research. If such men attended the meetings of the Society they would soon develop a taste for research, and would benefit accordingly. He appealed also to the leaders of physical science to attend the meetings, not for their own benefit, but from a sense of duty: for he was sure there was nothing so inspiriting to the younger members as contact with men who had carried out important work. He felt himself that any scientific spirit that he had acquired was due to personal contact in his early days with such men as Kelvin and his brother Thomson.

Dr. Chree, the President-elect, also responded to this toast, and in a humorous speech described how the membership of the Society might be increased, and how such things as logarithmic spirals might be impressed on the mind of the schoolboy.

In conclusion, The President proposed the health of the Honorary Secretaries, to which Mr. W. R. Cooper and Prof. W. Cassie responded.

NOTICES OF BOOKS.

Valentin's Practical Chemistry. By W. R. Hodgkinson. Tenth Edition. London: J. and A. Churchill. 1908.

In the tenth edition of this book some easy practical work has been introduced in the early chapters on the composition of air and water, diffusion, sulphur, and sulphuric acid, and some compounds of carbon, followed by elementary quantitative work, including both gravimetric and volumetric analysis, and methods of determining molecular weight. The reactions of the metals, arranged in analytical groups, are next treated, and general qualitative analysis schemes and tables are given. The new matter includes in addition discussions of the microscopical structure of some common alloys, illustrated by photographs, and the section on the properties and separation of the rare earths has been enlarged and brought up to date.

The Chemistry of Gas Manufacture. By Harold M. Royle, F.C.S. London: Crosby Lockwood and Son. 1907.

The chemistry of the making of gas is treated in outline in this book, which students who intend to take up the manufacture of coal-gas as a special study may find useful as an introductory course. Short accounts are given of the most accurate and rapid methods of testing both the raw materials and the products of gas works, and the experimental directions are sufficiently full for the use of a student who has some knowledge of general chemical analysis. Special attention has been paid to the numerical examples, typical analyses being carefully explained in detail. Photometric methods of testing gas are included, and appendices give the full official instructions for testing coal-gas, besides miscellaneous extracts of matter interesting to gas chemists from English and foreign periodicals.

The Law of Master and Servant. By T. C. Jackson, B.A., LL.B. London: Macdonald and Martin.

A succinct account of the law relating to master and servant is given in this book, which contains the full text of the Employers' and Workmen Act, 1875, the Employers' Liability Act, 1880, and the Workmen's Compensation Act, 1906. The interpretation of the Acts is made clear by short discussions of typical cases, and general principles are emphasised, while the tabulated form into which the information is thrown as far as possible makes the book very convenient for employers of labour to consult, in order to decide questions relating to their liabilities. The subject of apprenticeship is considered in one chapter, and another deals shortly with the law of the giving of testimonials and characters.

Syntheses by means of Methyl and Ethyl Adipates.—L. Bouveault and Locquin.—In this paper the authors give a list of the cyclopentanone derivatives of methyl and ethyl adipate, which can be prepared by the action of sodamide, NH_2Na, upon the adipates dissolved in anhydrous ether or in benzene, and enumerates their chief physical constants.—*Comptes Rendus*, cxlvi., No. 3.

CORRESPONDENCE.

HELIUM VACUUM TUBES.

To the Editor of the Chemical News.

Sir,—It is well known that helium vacuum tubes sooner or later become useless in consequence of the gradual absorption of the gas, and there must be hundreds of such tubes which have been thrown aside as no longer serviceable. A method of making such tubes useful again was suggested to me by the paper read at the Royal Society on November 7th by Soddy and Mackenzie. They found that on opening such tubes under mercury the greater part of the occluded gas was liberated by the action of the mercury on the film of volatilised aluminium. To put this to the test, a helium tube which had become useless was opened, a globule of mercury was introduced, and the tube was then exhausted and re-sealed. It showed at first only mercury lines, but on running the tube for a short time the helium suddenly flashed out, and the tube is now serviceable again for furnishing reference lines. For this purpose such a tube containing mercury is even better than a tube showing helium only, as the double yellow and green lines of mercury divide up an otherwise blank gap between yellow and green. The lines shown by the tube now are:—

Helium	6678·4
,, ...	5875·8
Mercury	5790·5
,, ...	5769·6
,, ...	5461·0
Helium	5015·7
,, ...	4922·1
,, ...	4713·3
,, ...	4471·6
,, ...	4388·8

and some others in the violet besides hydrogen, 6563·0 faintly.

On gently warming the tube its brilliancy increases considerably. Both helium and mercury lines became brighter, but on further heating the mercury lines became intensely brilliant at the expense of the helium lines, and at one stage the curious effect was produced of the upper half of the capillary illuminated by mercury, and the lower half by helium, so that in the spectroscope the lines belonging to mercury were picked out from those belonging to helium.—I am, &c.,

W. Marshall Watts.

Davy-Faraday Laboratory,
February 7th, 1908.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xli., No. 1, 1908.

Constitution of the Fatty Acid Salts of Beryllium.—B. Glassmann.—The fact that the action of acetic acid anhydride on beryllium acetate, Be_4Ac_6O, gives the normal beryllium salt, $(CH_3CO_2)_2Be$, is confirmation of the constitution which the author deduced for the fatty acid salts of beryllium. He has found that beryllium not only forms salts of the type Be_4Ac_6O, but also of the type Be_2Ac_2O with oxyacids and some haloid fatty acids, *e.g.*, beryllium lactate,—

$$CH_3.CH(OH).C<\begin{matrix}O\\O\end{matrix}>Be$$
$$O \qquad\qquad . H_2O.$$
$$CH_3.CH(OH).C<\begin{matrix}O\\O\end{matrix}>Be$$

Among other salts which, from their methods of formation, physical and chemical properties, and especially in their power of crystallising from acid solution, are to be regarded as ortho-salts, may be mentioned bismuthyl acetate, $BiO(CH_3{\cdot}CO_2)$; zirconyl tartrate, $ZrO(C_4H_4O_6)$; zirconyl acetate, $Zr(CH_3CO_2)_2O$, &c.

Carbon Suboxide.—Otto Diels and Paul Blumberg.—Diels and Wolf have explained the formation of carbon suboxide from malonic ester by supposing that a symmetrical reaction occurs. Thus:—

$$CH_2{<}^{CO_2C_2H_5}_{CO_2C_2H_5} = 2C_2H_4 + 2H_2O + C{\leqq}^{CO}_{CO} \quad . \quad . \quad I.$$

While Michael thinks that the compound is a β-oxypropiolic acid lactone,—

$$CH_2{<}^{CO_2C_2H_5}_{CO_2C_2H_5} = 2C_2H_4 + 2H_2O + C{\equiv}^{C}_{CO}{>}O \quad . \quad II.$$

If the formula is $C{\leqq}^{CO}_{CO}$ the calculated values for the molecular refraction and molecular dispersion are $M_D = 15{\cdot}49$, $\gamma - \alpha = 0{\cdot}749$; $\gamma - \alpha$ is the molecular dispersion for the red (α) and blue (γ) hydrogen line, while for $C{\equiv}^{C}_{CO}{>}O$ the corresponding values would be $M_D = 13{\cdot}57$, $\gamma - \alpha = 0{\cdot}435$. Thus the molecular dispersion of the substance of Formula I. is nearly double that of the substance of Formula II. Moreover, since, according to Brühl, in unsaturated heterocyclic ring systems there is a decided depression of the values of the refraction and dispersion, according to Michael's formula M_D and $\gamma - \alpha$ would be less than 13·57 and 0·435 respectively. The author's experiments, however, show that this is not the case. For M_D they have obtained the value 16·6, and for the dispersion in two series of experiments 0·736, 0·739, 0·862. This indicates that Michael's formula must be incorrect. It is interesting to notice that both the molecular refraction and dispersion of carbon suboxide found by experiment are high. Generally substances with the system $>C=C-C=<$ of double binding, show a decided "exaltation" of their molecular refraction and dispersion, while those with cumulated unsaturated atomic groups, *e.g.*, $CH_3{>}^{CH_3}C=C=CH_2$, are normal. Carbon suboxide belongs to a new type in which only double bonds are present, $O=C=C=C=O$, and in this also "exaltation" occurs.

Action of the Silent Electric Discharge on Damp Methane.—Walther Löb.—When methane saturated with water is exposed at the ordinary temperature to the action of a silent discharge, a white substance insoluble in all solvents is obtained. Simultaneously methyl esters of fatty acids are formed. The insoluble substance gives on analysis values which agree well with the formula $C_9H_{15}O$, or a polymer. All preparations of this insoluble substance contain traces of ash which consist of silicate. The appearance of higher aliphatic acids is easily explained if it is remembered that damp methane always undergoes the changes $CH_4 + H_2O = CO + 3H_2$ and $CO + H_2O = H.COOH = CO_2 + H_2$. The ethylene residues may then unite, and the following reactions occur:—$H.COOH + (CH_2{:}CH_2)_x = CH_3(CH_2)_{2x-1}.COOH$.

MISCELLANEOUS.

The British Association, Dublin Meeting, Sept. 2nd.—The following have been elected by the Council of the British Association to be presidents of sections at the meeting of the Association to be held in Dublin in September next under the general presidency of Mr. Francis Darwin, F.R.S.:—Section A (Mathematical and Physical Science), Dr. W. N. Shaw, F.R.S., Director of the Meteorological Office; Section B (Chemistry), Prof. F. S. Kipping, Professor of Chemistry in University College, Nottingham; Section C (Geology), Prof. J. Joly, F.R.S., Professor of Geology and Mineralogy in the University of Dublin; Section D (Zoology), Dr. S. F. Harmer, Superintendent of the University Museum of Zoology, Cambridge; Section E (Geography), Major E. H. Hills, C.M.G.; Section F (Economic Science and Statistics), Lord Brassey; Section G (Engineering), Mr. Dugald Clerk, M.Inst.C.E.; Section H (Anthropology), Prof. W. Ridgeway, Professor of Archæology in Cambridge University; Section I (Physiology), Dr. John Scott Haldane, F.R.S., University Reader in Physiology at Oxford; Section K (Botany), Dr. F. F. Blackman, F.R.S., Professor of Botany in the University of Leeds; Section L (Educational Science), Prof. L. C. Miall, formerly Professor of Biology in the University of Leeds. Invitations to deliver evening discourses during the meeting of the Association at Dublin have been accepted by Prof. H. H. Turner, F.R.S., Savilian Professor of Astronomy at Oxford, who will take as his subject "Halley's Comet"; and Prof. W. M. Davis, of Harvard University, whose lecture will be entitled "The Lessons of the Colorado Cañon."

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Biological Chemistry Examination.—I should be obliged if any reader would advise me as to best books from which to obtain the information necessary for the Examination in Biological Chemistry of the Institute of Chemistry.—P.

MEETINGS FOR THE WEEK.

Monday, 24th.—Royal Society of Arts, 8. (Cantor Lecture). "Theory and Practice of Clock Making," by H. H. Cunynghame, C.B.

Tuesday, 25th.—Royal Institution, 3. "Membranes—Their Structure, Uses, and Products," by Prof. William Stirling, M.A., LL.D., D.Sc., &c.

—— Royal Society of Arts, 4.30. "Irrigation in Egypt under British Direction," by Sir Hanbury Brown, K.C.M.G.

—— Faraday Society, 8. "Hydrolysis as Illustrated by Heats of Neutralisation," by V. H. Veley. "Study of the Sulphur Anion and of Complex Sulphur Anions," by J. Knox.

Wednesday, 26th.—Royal Society of Arts, 8. "Problem of Road Construction with a view to Present and Future Requirements," by H. S. Hele-Shaw, LL.D., F.R.S., and Douglas Mackenzie.

Thursday, 27th.—Royal Institution, 3. "Wood, its Botanical and Technical Aspects," by Prof. William Somerville, M.A., &c.

Friday, 28th.—Royal Institution, 9. "Explosive Combustion, with Special Reference to that of Hydrocarbons," by Prof. W. A. Bone, F.R.S.

—— Royal Society of Arts, 8. (Shaw Lectures on Industrial Hygiene). "The Removal of Dust and Fumes in Factories," by Dr. John Scott Haldane, F.R.S.

—— Physical, 5. "Contact Potential Differences Determined by means of Null Solutions," by S. W. J. Smith and H. Moss. "Experimental Examination of Gibbs' Theory of Surface Tension as the Basis of Adsorption, with an Application to the Theory of Dyeing," by Mr. Lewis.

Saturday, 29th.—Royal Institution, 3. "The Art of Florence," by Selwyn Brinton, M.A.

The Owner of BRITISH PATENTS No. 23841/05, entitled "Process for the Concentration of Sulphuric Acid," and No. 12538/06, entitled "Apparatus for Concentration of Sulphuric Acid," is desirous of DISPOSING of the Patents or entering into a working arrangement with firms likely to be interested in the same. The Patents cover inventions interesting to Chemical firms generally, and particularly to manufacturers of Sulphuric Acid.—Full particulars can be obtained from, and offers made to, Messrs. MARKS and CLERK, 18, Southampton Buildings, London, W.C., Agents for the Owner.

THE CHEMICAL NEWS.

Vol. XCVII., No. 2518.

THE ABSORPTION SPECTRA OF THE VAPOURS OF BENZENE AND ITS HOMOLOGUES AT DIFFERENT TEMPERATURES AND PRESSURES, AND LIKEWISE OF SOLUTIONS OF BENZENE.*

By WALTER NOEL HARTLEY, F.R.S., D.Sc.,
Royal College of Science, Dublin.

The author having been engaged since the year 1877 in investigating and correlating the physical and chemical properties of aromatic substances in relation to their chemical structure or constitution, he has latterly found it desirable that several very definite compounds should be examined in a state of vapour, as well as in solution.

The work of E. Pauer (*Annalen*, 1897, lxi., 363), W. Friederichs (*Zeit. f. Wissensehaftliche Photographie*, 1905, p. 633), and of L. Grebe (*loc. cit.*, 1905, p. 363) is referred to in detail. The vapours of benzene and several of its derivatives have been examined (1) at different temperatures and constant pressure; and (2) at different pressures, the temperature being constant. The previous measurements of Pauer, Friederichs, and Grebe have been confirmed, and reconciled where they do not show complete agreement with each other. The records of temperature and pressure, and the shortening of the exposure of the photographic plates, constitute important differences between the work of the former investigators and that of the author.

Details of the following photographs are given :—

Absorption Bands in the Spectrum of Benzene Vapour at different Temperatvres and a Barometric Pressure of 755·5 mm.

Temperatures.	Number of bands photographed and measured.
12·5°	55
25	84
43	82
53	56

Absorption Bands in the Spectrum of Benzene Vapour at 11·5° and different Pressures.

Pressures in mm.	Number of bands measured.
778	36
483	38
253	46
21	44

The same at 100° and different Pressures.

683	9
589	13
478	14
381	16
279	17
172	18

The same at 100°.

767	5
591	9
484	9
332	12
206	13
142	11
99	14
88	15

The same at 100°.

Pessures in mm.	Number of bands measured.
92	25
69	36
43	50

The same at 100°.

67·5	31
52·5	54
37·5	60
28·5	72
22·5	75
15·5	88
9	52
5	38
4	30

Absorption Bands in the Spectrum of Toluene Vapour at different Temperatures and constant Pressure.

Temperatures.	Number of bands measured
10°	16
30	20
40	16
50	20
60	23
70	21
80	24
90	23
100	18

The Absorption Spectrum of Toluene Vapour at different Pressures and constant Temperature.

Pressures in mm.	Number of bands measured.
763	18
563	16
371	18
174	15
43	15

The Absorption Bands of Ethylbenzene Vapour at different Temperatures.

Temperatures.	Number of bands measured.
16·5°	19
40	18
70	8
100	2

General absorption occurs here.

The same.

20	17
36	15
52	5
71	3
100	Complete absorption.

The Absorption Bands of o-*Xylene Vapour at different Temperatures.*

Temperatures.	Number of bands measured.
20°	23
45	21
72	
100	No bands, general absorption.
121	

Absorption Bands of m-*Xylene Vapour at different Temperatures.*

Temperatures.	Number of bands measured.
11°	26
40	41
70	6
100	5

General absorption occurs between 2652 and 2429.

* Abstract of a Paper read before the Royal Society, Dec. 12, 1907.

The same, *p*-Xylene Vapour.

Temperatures.	Number of bands measured.
10°	30
40	25
70 } General absorption from	5
100 } 2790 to 2416.	7

The same, Cymene Vapour.

17·5°	0
40	7
70	9
100	9

The same, Mesitylene Vapour.

18·5°	2
45	2
72	2
100	2
120 } General absorption.	
140 }	

The measurements are given of similar groups of bands which occur in the vapour-spectra of benzene, toluene, ethyl benzene, and the three isomeric xylenes; benzene and toluene being compared at ordinary temperatures and also at 30° below their respective boiling-points. A tabulated statement is also made of the heads of strong bands which appear to be common to benzene and its homologues. The intensities of the bands in the benzene vapour-spectrum at 100°, and different pressures, was compared with those at temperatures below its boiling-point, and it was seen that the bands at 100° are almost identical with those at lower temperatures, but with this difference, that, at lower temperatures, some of the bands at the less refrangible end of the spectrum are feeble and less well defined. The vapour-spectrum of benzene is divided into groups of bands which are caused by the overlapping of two or more similarly constituted spectra differing in intensity. The strong bands number fifty-four, there being twenty-seven in each of two spectra. In addition, there are thirty feeble bands, which also fall into two series of similar groupings, but with less regularity. The entire number of bands observed between 12·7° and 25°, under a pressure of 759·5 mm., are thus resolved into four spectra, of which two are composed of strong and two of weak bands.

Summary and Conclusions.

As regards the vapour-spectra, it is proved that benzene at 100° C. has the same molecular mass as at 25° or 12·7°.

The absorption bands at 100° are almost identical with those at lower temperatures, with variations as to definition in the less refrangible rays. The important influence of the position of the substituted hydrogens in benzene, upon the number and position of the bands in the spectra of its homologues, is clearly demonstrated.

Variations in the spectra of benzene at different temperatures and pressures are explained by the fact that there are two different kinds of absorption which are sharply defined and may be differentiated. First, there is the general absorption, which is broadened and extended towards the less refrangible rays by rise of temperature; secondly, there is the selective absorption, which includes all the narrow individual bands and groups of bands; they are not widened and displaced by rise of temperature, and such changes of this nature that they undergo are the effect of the overlying general absorption. The selective absorption is best studied by raising the general absorption to a maximum (at 100°), and studying the spectra produced by reduction of pressure. In this manner, any changes due to general absorption are eliminated. From the fact that increased sharpness and definition of the narrow bands is easily produced by rise of temperature, and also by reduction of pressure, the general absorption is clearly shown to be caused by encounters between the molecules, and the numerous narrow bands are to be ascribed to the vibrations of the atoms or atom-complexes within the molecules. This confirms the conclusion drawn from the study of solution-spectra published in 1881 (*Journ. Chem. Soc.*, xxxix., p. 153), in 1882 (*loc. cit.*, xlvii., p. 685), and 1885 (*Phil. Mag.*, 1885, [5], xix., p. 35).

The similar groups of bands occurring in benzene and toluene, and the close similarity between the spectra of toluene and ethylbenzene, with the further resemblance between *m*-xylene and toluene and ethylbenzene, is evidence that the mode of vibration within the benzene nucleus or ring-structure is in a great measure unaffected by the side-chain substitution.

A distinction is drawn between the absorption spectra of vapours, called *vapour-spectra*, and of solutions, called *solution-spectra*, and the relationship of one to the other is explained. Previous investigations carried on by the author for many years are briefly referred to, and it is shown how the views entertained have been confirmed by the investigation of the *vapour-spectra*. Attention is drawn to the insufficiency of ordinary chemical formulæ to represent the constitution of organic compounds, particularly of those like benzene which are of an endothermic character, since they do not take into account the distribution of energy in the molecule, and this obscures the view of the physical character of chemical structure or constitution. In short, whereas bonds and linkings in the formulæ usually written belong to a conception of chemical structure which is statical, the molecular constitution of such substances as are under discussion, when based upon the evidence derived from their optical properties, is essentially dynamical. ("Single, double, or treble linkings are simply an incomplete method of representing the relation of the carbon-atoms to each other at some particular phase of their vibrations," *Phil. Mag.*, 1885, xix., p. 55). The relation of *solution-spectra* to *vapour-spectra* is shown, by reference to the results obtained by Pauer, Hartley and Dobbie, and by Grebe. The view entertained by Baly and Collie (*Chem. Soc. Trans.*, 1905, lxxxvii., p. 1332) that benzene has seven and no more than seven *solution-bands*, indicative of a definite making and breaking of a double linkage of the carbon atoms in the ring, has been carefully examined, and the author finds this to be incompatible with well-ascertained facts. From the measurements and numerical relations of the wave-lengths of bands in *solution-* and *vapour-spectra*, it is explained how four, six, seven, eight, or nine bands may be recognised in *solution-spectra*, six of which are similarly constituted, and four of these are not only similarly constituted but very nearly of equal width, intensity, and persistency; that is to say, they have the same coefficient of extinction, and in all other respects an almost exact similarity. They correspond with four groups of *vapour-bands* which are formed by the four different series of bands which overlap, and they occur where they overlap to the greatest extent.

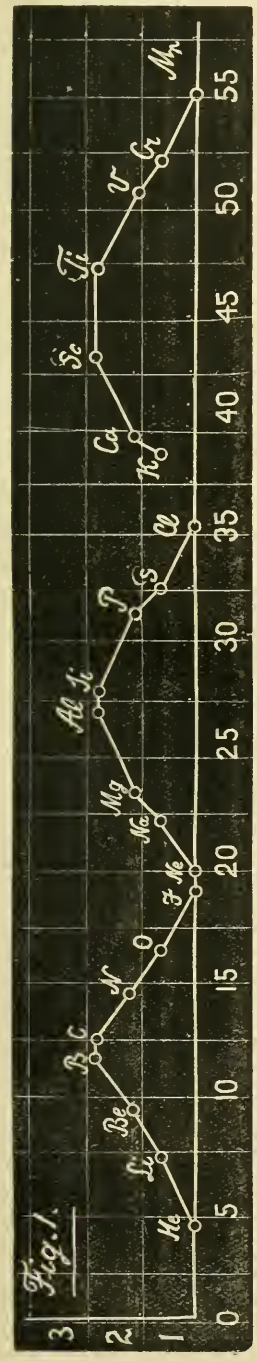
Density of Graphite. — H. Le Chatelier and S. Wologdine. — The authors have performed a series of determinations of the density of graphite, using mixtures of acetylene bromide and ether. The specimens were subjected to a careful purification, and the results showed that both natural and artificial graphites when perfectly pure have a density of 2·255 (water at 4°), the mean temperature of the graphite being 15°.—*Comptes Rendus*, cxlvi., No. 2.

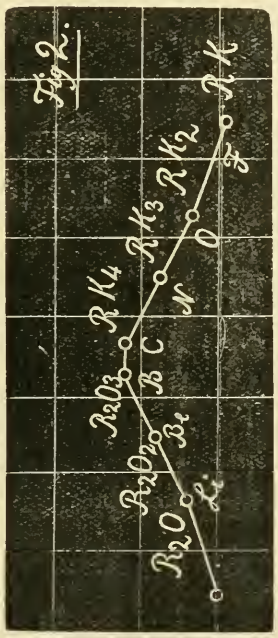
Royal Institution.—On Thursday next, March 5, at 3 o'clock, Prof. Sir John Rhys begins a course of two lectures at the Royal Institution on "Early British History and Epigraphy," and on Saturday, March 7, Prof. J. J. Thomson commences a course of six lectures on "Electric Discharges through Gases." The Friday Evening Discourse on March 6 will be delivered by Prof. John Milne on "Recent Earthquakes," and on March 13 by Chevalier G. Marconi on "Transatlantic Wireless Telegraphy."

ON THE SYMMETRY IN THE LAW OF ATOMIC WEIGHTS.

By Prof. Dr. N. DELAUNAY.

IN the diagram (Fig. 1) the abscissæ represent the atomic weights of the chemical elements, and the ordinates of the elements are 0, 1, 2, 3; 3, 2, 1, 0; and so on. The diagram, if prolonged to uranium, represents the law of Mendeleeff, because the elements having the same ordinates in ascending branches form a group; for example, Li, Na, K . . . The elements, having the same ordinate in descending branches, also form a group; for example, O, S, Cr . . . Each wave of the curve represents the valency as in Fig. 2. Each wave has an individual character, and the details of the numerical properties of the system are apparent in the diagram, Fig. 1.





But the chief point of interest presented by our diagram consists in the new and unexpected fact, *the complete symmetry of the first and the second waves, and the symmetry of the upper part of the third wave.*

This symmetry causes the sum of the numbers equidistant from the ends of each period to be constant, as follows:—

He + F = 4 + 19 = 23	Ne + Cl = 20 + 35·45 = 55·45
Li + O = 7 + 16 = 23	Na + S = 23 + 32·07 = 55·12
Be + N = 9 + 14 = 23	Mg + P = 24·48 + 31·02 = 55·30
B + C = 11 + 12 = 23	Al + Si = 27·11 + 28·40 = 55·51

Ka + Cr = 39·11 + 52·14 = 91·25
Ca + V = 40·07 + 51·38 = 91·45
Sc + Ti = 44·12 + 48·15 = 92·27

Kief, December 28, 1907.

THE ELECTROLYTIC DEPOSITION OF ZINC, USING ROTATING ELECTRODES.*

II.

By T. SLATER PRICE, D.Sc.

(Concluded from p. 90).

Experiments Using the Rotating Cathode (continued).

THE results shown above are very satisfactory, and confirm the statement in the previous paper that good results are obtained in the presence of 2 grms. of sodium sulphate plus 1 grm. of sodium acetate, the addition of free acetic acid being unnecessary. If no acid is added the electrolyte is slightly cloudy, because of the precipitation out of a trace of zinc hydroxide, but this cloudiness disappears immediately the current is started; it does not seem to bring about the deposition of spongy zinc, which would affect the result. In all cases the deposits were firm and adherent and of a light grey colour, and no zinc was left in solution, as indicated by the ferrocyanide test. It will be noticed that coppering the electrode has the same effect as silvering it. The deposition potential of zinc is altered when it is deposited on a metal with which it alloys readily (*cf.*, Spitzer, *Zeit. Elektrochem.*, 1905, xi., 345), and it may possibly become lower than that of hydrogen, or at all events close to it. The formation of spongy zinc would thus be avoided. This, however, is a point for further investigation. Coehn (*Zeit. Phys. Chem.*, 1901, xxxviii., 612), using a solution of sodium zincate, finds that the deposition potential of zinc on platinum cathodes is lower, by about 0·02 volt, than on cathodes of gold, silver, and copper. He states that this is due to the ease with which zinc alloys with platinum. This is contrary to what one would expect, since zinc alloys more readily with silver and copper than with platinum.

In all the above determinations the number of revolutions per minute of the cathode was 600—700. Table III. shows that from a speed of about 300 revolutions per minute onwards the results are satisfactory. In each case the electrolyte contained 2 grms. of sodium sulphate and 1 grm. of sodium acetate; the current was 2 amps. and the time of electrolysis fourteen minutes.

* A Paper read before the Faraday Society, March 19, 1907,

Table III.

Revolutions per minute	240	460	690	860
Per cent Zn..	22·70	22·73	22·75	22·74
Error	−0·04	−0·01	+0·01	0·00

In the first case the deposit was not a good one, so that 240 revolutions per minute is not a safe speed to work at.

That fourteen minutes afford ample time for the deposition of the zinc from 1 grm. of zinc sulphate is shown by Table IV. The number of revolutions was 600—700, and the other conditions, with the exception of the time, as given above.

Table IV.

Time (in minutes) ..	10	12	14	22
Per cent Zn..	22·44	22·74	22·73	22·75
Error	−0·30	0·00	−0·01	+0·01

There is one point to notice in connection with the drying of the deposit of zinc after washing it with alcohol. In all cases this was done in the steam oven. Foerster, in a recent paper in the *Zeit. Angew. Chemie*, 1906, xix., 1842, states that the deposit (of zinc) was dried carefully over the bare flame. This latter method, which is commonly used in drying a number of electrolytic deposits, is likely, in the case of zinc, to lead to high results, owing to the products of combustion of the gas acting on the zinc. In a series of experiments which I made the deposit was dried in an air oven at 100°—110° C. The results were always high, and varied greatly among themselves. It was afterwards found that the bottom of the oven was faulty, and that the waste gases from the burner got into the oven and acted on the deposit, discolouring it slightly.

Tables V. to VIII. give the results obtained, using different electrolytes. The number of revolutions per minute of the cathode was in all cases 600—700.

Ammonium Sulphate and Ammonia.—In each case 3 grms. of ammonium sulphate were used (Table V.). In every case, with the exception of the first, the zinc was completely deposited. The deposit was dark in colour, and decidedly crystalline. The results are uniformly high, but the error is very small. Satisfactory results for zinc in the presence of ammonia do not seem to have been obtained previously.

Table V.

Cc. of 0·880 ammonia.	C.	V.	*t.*	Per cent Zn.	Error.
0·75 (*a*)	2	4—5	14	21·28	−1·46
1·5	2	4—5	20	22·79	+0·05
1·5 [10]	2	—	20	22·82	+0·08
2	2	4—5	20	22·77	+0·03
2	2	—	14	22·78	+0·04
5	2	—	20	22·80	+0·06

(*a*) This volume of ammonia was slightly more than that necessary to dissolve the precipitate first formed.

Caustic Soda.—Four grms. of caustic soda were used in each case (Table VI.). In each case the zinc was completely deposited, but the deposit was very dark in colour, although firm and adherent. It does not appear to affect the result whether the solution be electrolysed in the cold or previously heated to boiling. Exner (*Journ. Am. Chem. Soc.*, 1903, xxv., 896) and Ingham (*Journ. Am. Chem. Soc.*, 1904, xxvi., 1269), using a rotating anode, recommend the adoption of the latter course. When a solution containing 4 grms. of caustic soda, without any zinc sulphate, was electrolysed for twenty minutes, the alteration in weight of the cathode was −0·0001 grm., *i.e.*, within the error of experiment. The high results are therefore not due to impurities in the caustic soda.

Table VI.

C.	V.	*t.*	Per cent Zn	Error.
2	3·5	20	22·83	+0·09
2	3·75	20	22·88	+0·14
0·5 (5), 1 (10), 2 (10)	2·5—4	25	22·79	+0·05
2 (*a*)	2·5—3	20	22·87	+0·13
2 (*a*)	2·5—3	19	22·88	+0·14

(*a*) In these cases the solution was heated to boiling, by means of a ring burner arranged under the funnel, before the electrolysis was commenced.

Sodium Acetate and Acetic Acid.—Exner and Ingham both recommend that the solution be heated to boiling before the electrolysis is commenced. Using a rotating cathode, the results, when such a course is adopted, are not satisfactory (see Table VII.). Even in the last case, where the error appears to be very small, some zinc was left in solution. Using cold solutions, the deposition is complete, giving an adherent deposit somewhat darker in colour than when some of the acetate is replaced by sulphate. The results, although they are uniformly high, are more satisfactory than those given in the previous paper; the error is small.

Table VII.

Grms. of Na acetate.	Drops of glacial acetic acid.	C.	V.	*t.*	Per cent Zn.	Error.
3	2	2	6—6·5	14	22·79	+0·05
3	2	2	6·5—7	14	22·79	+0·05
3	2	0·5 (5), 1 (10), 2 (10)	3·5—7	25	22·79	+0·05
2	—	2	6·5—7	14	22·81	+0·07
3 (*a*)	2	2	3·4—4·5	14	22·64	−0·10
5 (*a*)	2	2	3—3·5	14	22·73	−0·01

(*a*) Solution boiled before the electrolysis was commenced.

Ammonium acetate as electrolyte gave very dark deposits and high results, as, for instance, 23·85 per cent.

Sodium Sulphate (Table VIII.).—In the previous communication it was stated that good results could be obtained using sodium sulphate alone as an electrolyte. Further investigation has shown, however, that the method is not satisfactory and that the results are uncertain. Occasionally one obtains good results, but they seem to depend too much on fortuitous circumstances, such as the position of the cathode with respect to the anode. If the former is fixed too low down, the zinc which is first deposited on the lower portion is dissolved off towards the end of the experiment.

Table VIII.

Grms. of Na_2SO_4.	C.	V.	*t.*	Per cent Zn.	Error.
5	2	5—5·5	14	22·30	−0·44
3	0·5 (2), 1 (2), 2 (15)	6	19	22·63	−0·11
3	0·5 (3), 1 (3), 2 (15)	—	21	22·51	−0·23
3	0·5 (2), 1 (2), 2 (15)	—	19	22·45	−0·29

In one experiment 2 cc. of ammonia were added ten minutes after the commencement of the electrolysis; after ten minutes more all the zinc had been deposited, giving as the result 22·78 per cent.

A few experiments were done, using no extraneous electrolyte and cooling with ice, as described in the previous paper. When the electrode was not previously silvered the results were very unsatisfactory—*e.g.*, 22·67, 22·43, and 21·21 per cent. When the electrode was silvered the results were 22·67 and 22·73 per cent. Here again, however, an extended experience has shown that the results depend to a great extent on the position of the cathode, so that the method could not be used for the ordinary quantitative determination of zinc, for which, as a matter of fact, it was never intended. Traces of zinc are very liable to be left in solution.

Experiments using a Mercury Cathode and Rotating Anode.

It has been stated that the method of Kollock and Smith, using a mercury cathode and rotating anode, was always found to give low results (in the case of zinc). A number of experiments were therefore made to find out the cause of this. In order to obtain results comparable with those of Kollock and Smith their method of working was adopted, *i.e*, the electrolysis tube containing the mercury (or amalgam) was weighed complete, and not simply the mercury or the amalgam resulting from the electrolysis.

Some of the results obtained are given below. In every case the mercury (or amalgam) was washed three times with each of the following liquids: water, absolute alcohol, and dry, freshly distilled ether. The mercury used had been previously purified by distillation. Six drops (40 drops = 1 cc.) of concentrated sulphuric acid were added; the current was 5 ampères, the voltage 7, and the time allowed for electrolysis fifteen minutes—much longer than was really necessary. Before being weighed, the apparatus was allowed to stand in the balance case at least twenty minutes.

Per cent Zn.	Error.
22·63	−0·11 (*a*)
22·67	−0·07
22·77	+0·03
22·59	−0·15
22·65	−0·09
22·61	−0·13
22·54	−0·20

(*a*) Six washings each with alcohol and ether, three with water.

With one exception, and that the only one out of fifty or more determinations, the results are low. A glance at Kollock and Smith's figures shows that their results were sometimes high and sometimes low. The reason of this discrepancy may possibly be as follows:—In order to dry the amalgam (or the mercury) after it had received the final washing with ether, it was put into a desiccator, which, in my experiments, was then evacuated. Kollock and Smith do not say whether the desiccator was evacuated or not, so presumably it was not; the results would then be liable to error, as shown by the following figures: The weight of the tube plus amalgam after being in the desiccator for two hours (no vacuum) was 73·4114 grms. The tube with its contents was again put into the desiccator, which was then evacuated. During the process of evacuation bubbles, presumably of ether vapour, could be seen escaping from the surface of the amalgam. The weight after this treatment was 73·4088 grms., a loss in weight of 2·6 mgrms. In another experiment, even after drying in a desiccator (no vacuum) for five hours, the weights were 74·4473 and 74·4468 grms. respectively, so that under the conditions used by Kollock and Smith it would take a very long time before the weight became constant. It may be objected that mercury would lose in weight in the vacuum desiccator; that this is not so is shown by the following figures:—

Time in vacuum desiccator (hours)	0	3	24	41
Weight of tube and mercury (grms.)	70·2163	70·2163	70·2161	70·2158

The low results are not due to the deposition of the zinc being incomplete. In all cases the liquid syphoned off before the current was stopped showed no trace of zinc.

On testing the washings obtained during the treatment of the amalgam after the current had been stopped it was found that both those with water and those with alcohol showed the presence of a trace of zinc. The amount was too small to be estimated, but rough tests indicated that it was not enough to account for the low results. Further investigation showed that the action of water on zinc amalgam is fairly rapid; if the latter is allowed to stand in contact with water for a few hours it becomes coated with a layer of zinc hydroxide, and the water readily responds to the ferrocyanide test for zinc.

It is possible that during the washing of the amalgam some of it is mechanically carried away. To test this a weighed quantity of amalgam was repeatedly subjected to the same treatment as in the actual determination, *i.e.*, three washings each with water, alcohol, and ether respectively, and drying in a vacuum desiccator. The successive weighings obtained were 67·1313, 67·1286, 67·1234 grms., *i.e.*, a decrease in weight after each set of operations. It was especially noticeable during the washing with ether that the surface film of the amalgam broke up, and portions of it were mechanically carried away. Even if pure mercury is washed with ether a black scum, presumably of mercury, is formed, which gives the mercury a very dirty appearance, and is mechanically carried away as the washing is proceeded with. A series of tests with mercury alone, washing with water, alcohol, and ether, gave the following weighings: 66·8966, 66·8948, 66,8946, 66·8928, 66·8915, 66·8892, and 66·8872 grms. respectively—again a decrease after each operation. The amalgam and mercury used in these tests were cold. In the actual determination of zinc, if it was observed that any amalgam was mechanically carried away—and that very seldom happens—the results of the experiment were rejected. The amalgam gets very hot during the electrolysis, and the surface film does not form so readily then as when cold. The chemical action of the amalgam on water would be accelerated by rise in temperature.

In order to diminish the time necessary for washing the amalgam, as well as the number of operations, a series of experiments were carried out to see if the washings with ether, or even with ether and alcohol, could be avoided. It was then necessary to dry the amalgam in the air oven at 100—110° C. Under these conditions the amalgam does not lose in weight by volatilisation of mercury, as shown by the following figures:—

Duration of heating (mins.).	Weight (grms.)
0	76·0570
35	76·0569
0	73·2869
35	73·2869
0	61·4821
60	61·4818

Mercury alone, under these conditions, loses considerably in weight. In the acual determinations the amalgam was heated just long enough to dry it. Some of the results are given in Table IX.

Table IX.

Number of washings given with—		Per cent Zn.	Error.
Water.	Alcohol.		
3	3	22·59	−0·15
3	3	22·61	−0·13
6	6	22·62	−0·12
12	12	22·52	−0·22
1	3	22·55	−0·19
1	3	22·61	−0·13
—	6	22·52	−0·22
—	6	22·65	−0·09
3	—	22·70	−0·04
3	—	22·62	−0·12
6	—	22·60	−0·14

The results are no better than when ether, in addition to water and alcohol, is used. It is somewhat difficult to draw considerations from them, since they are so very irregular. One might perhaps be inclined to say that an increase in the number of washings increases the error, but it must be admitted that there is considerable irregularity, which is perhaps to be expected, since it is impossible

to keep the conditions under which the washings are carried out the same.

If any mercury is carried away, either mechanically or chemically, it should be possible to prove its presence in the washings. This was done as follows (*cf.*, Fresenius, "Qual. Analysis," 10th edit., p. 145) :—Six determinations of zinc were carried out in the manner already described, three washings with water and three with alcohol being given in each case. The washings were collected (no globules of mercury could be seen in them) and evaporated down on the water-bath to a small bulk, small quantities of nitric and sulphuric acids having previously been added. The solution so obtained was electrolysed over night, using a platinum anode and a small cathode of pure copper. The cathode was afterwards washed and dried and put into a piece of combustion tubing, which was then drawn out to a capillary on either side of the copper. The part of the tubing containing the copper was heated to a low red heat for some time. After cooling a film could be seen in each of the capillaries and examination with the microscope showed it to consist of opaque globules. A small amount of iodine was brought into contact with one of the films, and the whole gently warmed. A yellow deposit resulted, which, under the microscope, was seen to consist of a number of yellow crystals, with a few scarlet ones interspersed. On standing for some time the yellow crystals gradually became scarlet in colour. There is thus no doubt that the film was mercury, which must have come from the washings. Whether it is mechanically carried away or chemically dissolved during the washing remains undecided.

The above results seems to show that the uniformly low results obtained by Kollock and Smith's method for the estimation of zinc are due to loss of zinc and mercury during the washing of the amalgam.

(These results, of course, only hold for zinc, which is never so satisfactory to deposit electrolytically as most of the other metals).

Since the publication of the first paper on the electrolytic determination of zinc the suggested alteration of Kollock and Smith's method, in which the amalgam is run off through a tap funnel, has been tried by various workers in this laboratory. It has not been found to be as satisfactory as, at first trial, it seemed to be. An error is likely to arise from the splashing of the mercury when poured into the funnel ; this is easily obviated by putting some water into the latter before the mercury is poured in. The water can then be pipetted off before the solution of zinc sulphate is run in. If the electrolyte is syphoned off and replaced by distilled water before running off the amalgam, portions of the latter are liable to stick to the sides of the funnel, and thus vitiate the result. The better method is to run off the amalgam directly, without syphoning off the electrolyte ; but even then it requires some practice before this can be done successfully, *i.e.*, so that the amalgam runs off dry. In most cases a drop of the electrolyte follows the amalgam, which has then to be washed, although not so thoroughly as with the usual method, since the drop of electrolyte lies on the surface of the amalgam. This drop contains sulphuric acid, and consequently some of the amalgam is decomposed. Any appreciable decomposition of the amalgam while actually in the leg of the funnel and not in contact with the electrode (the negative leading wire is bent down into the part of the leg above the tap) is obviated by the fact that a bubble of gas collects between the amalgam and the electrolyte and prevents further decomposition. That, in practised hands, the method gives quite as good results as the ordinary one is shown by the following results: 22 69, 22·66, 22·66, 22·66, 22·69 per cent Zn.

The results communicated in the present paper seem to indicate that the most satisfactory method for the electrolytic deposition of zinc is that in which a rotating cathode is used, the electrolyte consisting of a solution of 2 grms. of sodium sulphate and 1 grm. of sodium acetate to each grm. of zinc sulphate.

A NEW METHOD OF DETERMINING VAPOUR DENSITIES.*

PART I.

By PHILIP BLACKMAN.

THE apparatus used for this method consists of a long glass bulb, with a glass stopper at one end, and at the other end a capillary tube also carrying a tap. Two threads of mercury are introduced, one to close the tap, the other near the bulb to form an air manometer. A weighed quantity of the substance to be experimented on is introduced in a small tube, the stopper fixed and wired on, and the apparatus heated in the vapour of a liquid boiling at a temperature above that at which the substance vaporises. A small quantity of mercury must also be introduced into the bulb to aid in sealing it. Let p = atmospheric pressure and $t_1°$ = temperature of the apparatus when the substance of weight, w, was introduced ; V = volume of the bulb ; $t_2°$ = temperature of the vapour ; L, l = volumes of the air-gauge at $t_1°$ and $t_2°$ respectively ; H, h = respective volumes of the space in the capillary between the bulb and the mercury at $t_1°$ and $t_2°$; the vapour density compared with hydrogen at 0° and 760 mm. is given by Formula I., or (as H and h are very small compared with V) Formula II. The apparatus gives excellent results quickly and with ease :—

$$\frac{31068\,wl\,(273 + t_1)}{p(V + h)\left(L - l\,\frac{V + H}{V + h}\right)} \quad . \quad . \quad . \quad . \quad . \quad \text{I.}$$

$$\frac{31068\,wl\,(273 + t_1)}{pV\,(L - l)} \quad . \quad . \quad . \quad . \quad . \quad \text{II.}$$

I must tender my thanks to R. Blair, Esq., Executive Officer of the L.C.C., and to the authorities of the Hackney Technical Institute, Dalston Lane, N.E., for the facilities granted me in carrying out the research.

THE REACTION BETWEEN POTASSIUM-ALUMINIUM SULPHATE AND A BROMIDE-BROMATE MIXTURE.

By F. A. GOOCH and R. W. OSBORNE.

WHEN the water solution of a neutral aluminium salt is boiled, hydrolysis may take place until an equilibrium is brought about between the free acid formed and other active products. If a product is inert toward the acid set free in the liquid, or if the acid is continuously removed or destroyed, the process goes on until no further hydrolytic action is possible under the conditions.

In the basic acetate process for the separation of alumina, the insoluble aluminium compound is a basic salt inert toward the free acetic acid formed under the conditions.

In Chancel's method of precipitating alumina, by the action of sodium thiosulphate upon the boiling solution of the soluble aluminium salt, the insoluble product is likewise a basic salt, in this case the sulphate, and the sulphuric acid set free is fixed as sodium sulphate, while the thiosulphuric acid formed in metathesis is destroyed at the temperature of the reaction with formation of the comparatively inactive sulphur dioxide and sulphur ; though, as Norton has shown, the basic salt is not quantitatively insoluble until the mixture is superheated under pressure (*Ber.*, 1900, xxxiii., 548).

In Stock's process (Norton, *Am. Journ. Sci.*, 1901, xii., 118) for the determination of alumina, aluminium sulphate in solution is heated at the boiling temperature with a

* Abstract of a Paper read before the Chemical Society, January 16, 1908. Compare CHEMICAL NEWS, 1907, xcvi., 223 ; *Journ. Chem. Soc.*, 1907, xcii., Abs. II., 931.

TABLE I.

	$KAl(SO_4)_2.12H_2O$ taken. Grms.	Time of heating. Hours.	KBr taken. Grms.	$KBrO_3$ taken. Grm.	Al_2O_3 taken. Grm.	Al_2O_3 found. Grm.	Error. Grm.
1.	1·0012	1·0	3·6	1·0	0·1078	0·1070	−0·0008
2.	0·5017	2+2·5	2·0	0·5	0·0539	0·0529	−0·0010
3.	0·5029	3+2·5	2·0	0·5	0·0541	0·0559	+0·0018

TABLE II.

No.	Time. Hours.	$KAl(SO_4)_2.12H_2O$ taken. Grm.	KBr used. Grms.	$KBrO_3$ used. Grm.	Bromine liberated. Grm.	Theory for bromine. Grm.	Error in terms of bromine. Grm.	Error in terms of Al_2O_3. Grm.
			A.—Theory: 6Br to $2KAl(SO_4)_3.12H_2O$.					
1.	0·5	0·5000	1·8	0·5	0·2052	0·2527	−0·0475	−0·0101
2.	1·5	0·5000	2·16	0·6	0·2064	0·2527	−0·0463	−0·0097
3.	2·0	0·5000	2·16	0·6	0·2084	0·2527	−0·0443	−0·0094
4.	2·5	0·5000	2·16	0·6	0·2099	0·2527	−0·0408	−0·0091
5.	3·5	0·5000	2·16	0·6	0·2119	0·2527	−0·0408	−0·0087
6.	4·0	0·5000	2·16	0·6	0·2120	0·2527	−0·0407	−0·0086
			B.—Theory: 5Br to $2KAl(SO_4)_2.12H_2O$.					
1.	0·5	0·5000	1·8	0·5	0·2052	0·2106	−0·0054	−0·0011
2.	1·5	0·5000	2·16	0·6	0·2064	0·2106	−0·0042	−0·0009
3.	2·0	0·5000	2·16	0·6	0·2084	0·2106	−0·0022	−0·0005
4.	2·5	0·5000	2·16	0·6	0·2099	0·2106	−0·0007	−0·0001
5.	3·5	0·5000	2·16	0·6	0·2119	0·2106	+0·0011	+0·0002
6.	4·0	0·5000	2·16	0·6	0·2120	0·2106	+0·0014	+0·0003

TABLE III.

	Time. Hours.	$KAl(SO_4)_2.12H_2O$. taken. Grm.	KBr taken. Grms.	$KBrO_3$ taken. Grms.	Theory for bromine. Grm.	Bromine found. Grm.	Error in terms bromine. Grm.	Error in terms Al_2O_3. Grm.
			A.—Theory: 6Br to $2KAl(SO_4)_2.12H_2O$.					
1.	3	0·5000	0·32 (*a*)	0·09 (*a*)	0·2527	0·1437	−0·1090	−0·0232
2.	3	0·5000	3·2	0·09	0·2527	0·1814	−0·0713	−0·0152
3.	3	0·5000	0·32	0·90	0·2527	0·1853	−0·0674	−0·0144
4.	3	0·5000	3·2	0·90	0·2527	0·2182	−0·0345	−0·0073
5.	3	0·5000	6	2	0·2527	0·2199	−0·0328	−0·0069
6.	4	0·5000	6	2	0·2527	0·2229	−0·0298	−0·0063
7.	5	0·5000	6	2	0·2527	0·2320	−0·0207	−0·0044
			B.—Theory: 5Br to $2KAl(SO_4)_2.12H_2O$.					
1.	3	0·5000	0·32 (*a*)	0·09 (*a*)	0·2106	0·1437	−0·0669	−0·0143
2.	3	0·5000	3·20	0·09	0·2106	0·1814	−0·0292	−0·0062
3.	3	0·5000	0·32	0·90	0·2106	0·1853	+0·0252	−0·0054
4.	3	0·5000	3·2	0·90	0·2106	0·2182	+0·0076	+0·0016
5.	3	0·5000	6	2	0·2106	0·2199	+0·0090	+0·0019
6.	4	0·5000	6	2	0·2106	0·2229	+0·0123	+0·0026
7.	5	0·5000	6	2	0·2106	0·2330	+0·0214	+0·0045

(*a*) These amounts are nearly equivalent to the acidic ion of the aluminium salt.

mixture of potassium iodide and potassium iodate. The sulphuric acid produced hydrolytically is fixed by the iodide-iodate mixture, and comparatively inert iodine is set free and taken up by sodium thiosulphate to form sodium iodide and sodium tetrathionate. In this process, as Moody has shown (*Am. Journ. Sci.*, 1905, xx., 181), the first insoluble product is a basic salt; but prolonged boiling of the mixture of aluminium sulphate, potassium iodide, and potassium iodate finally brings about the complete hydrolysis of the insoluble basic salt, so that the entire amount of iodine set free in the process, when properly collected and titrated, may serve as an accurate measure of the acid produced and therefore of the acidic ion of the aluminium salt.

In an extension of this process to other elements Moody found that a sufficiently prolonged treatment with the iodide-iodate mixture completely liberated the acidic ion from the sulphates of iron, chromium, cobalt, nickel, ammonium, and from stannic chloride. The hydrolysis of zinc sulphate under similar conditions comes to an end before the acidic ion is entirely liberated and when the product is one-fifth sulphate and four-fifths hydroxide.

In the work of which the present paper is an account, the reaction of a mixture of potassium bromide and potassium bromate upon aluminium sulphate has been studied. Assuming that the acidic ion is entirely liberated from the aluminium salt, the reaction should follow the equation—

$$2KAl(SO_4)_2+5KBr+KBrO_3+3H_2O=$$
$$=2Al(OH)_3+4K_2SO_4+3Br_2.$$

For this work a bromide-bromate solution was made up by dissolving 36 grms. of potassium bromide and 10 grms. of potassium bromate (the proportions indicated in the equation) in water and making up to 500 cc. Pure crystallised potassium alum was the aluminium salt used, and this was weighed out exactly in every experiment.

The first set of experiments (Table I.) was made to find out whether precipitation is complete when the bromide-bromate mixture acts upon the aluminium salt. In every experiment a portion of the alum was weighed out, dissolved in a small amount of water in a beaker, and a portion of the bromide-bromate solution was added. In Experiment 1 the mixture was boiled over a flame until at the end of an hour no more bromine seemed to be liberated

and the cooled liquid was colourless. The precipitate was, so far as possible, transferred to an ashless filter-paper, washed, ignited, and weighed as Al_2O_3; but to get the entire amount of precipitate it was necessary to dissolve from the beaker, by means of hydrochloric acid, a closely adherent film of precipitate; and from the solution the dissolved alumina was recovered by precipitation with ammonia and determined separately. In Experiments 2 and 3 the precipitation was brought about by passing a current of steam into the solution, interrupting the process to concentrate the liquid by evaporation without boiling, and again passing in steam.

In these experiments the precipitation proved to be complete, or nearly so; though in No. 3 there is obvious contamination of the precipitate, due perhaps to the prolonged treatment in glass. As will appear, however, the process of hydrolysis did not go to the point of forming aluminium hydroxide.

The degree to which the acidic ion is removed hydrolytically from the salt under the conditions is shown in the following series of experiments (Table II.), in which portions of the alum were treated with the bromide-bromate mixture under conditions which permitted the collection and titration of the bromine set free in the reaction.

The apparatus used consisted of a Voit flask, used as a distilling flask, sealed to the inlet tube of a Drechsel wash-bottle, used as a receiver, to the exit tube of which was sealed a Will and Varrentrapp absorption tube. The Voit flask was charged with 0·5 grm. of alum dissolved in a little water and 25 cc. or 30 cc. of the bromide-bromate mixture. The solution was boiled for the time indicated and the bromine liberated passed in a current of hydrogen, sent through the whole apparatus, to the receiver containing in the cylinder and trap a solution of 4 grms. of potassium iodide in 200 cc. of water. The iodine set free by the action of the bromine liberated in the reaction was titrated by *n*/10 sodium thiosulphate with the aid of a starch indicator.

From these experiments, in which approximately three times the amounts of potassium bromide and potassium bromate, corresponding to the complete hydrolysis of the alum, were used, it is obvious that the hydrolysis is not complete. At the end of an hour nearly five-sixths of the acidic ion have been liberated, and this proportion is not much exceeded after four hours boiling, the liberation of bromine proceeding very slowly during the greater part of this time.

In the series of determinations given in Table III. the proportions of potassium bromide and potassium bromate with reference to one another and to the aluminium salt were varied in order to test the effect of such variation on the course of the action.

In the result of Experiment 1, in which the amounts of bromide and bromate were equivalent to one another and to the acidic ion of the aluminium salt, it will be noted that the liberation of the bromine falls considerably short of five-sixths of the equivalent of the acidic ion. In Experiment 2 the bromide was increased tenfold, and in Experiment 3 the bromate tenfold with similar though incomplete effects. In Experiment 4, in which both the bromide and the bromate amount to ten times the theoretical equivalent of the acidic ion, the results show a liberation of bromine somewhat in excess of the five-sixths proportion. In Experiments 5, 6, 7, further increase in the amounts of bromide and bromate and in the time of boiling advanced the reaction so that amounts of bromine were liberated considerably in excess of the five-sixths proportion. These results seem to indicate that the deficient hydrolytic effect is advanced by large increase in the proportions of either the bromide or the bromate or both, and would seem to confirm the natural inference that the products of the action of the bromide and the bromate upon aluminium sulphate take part essentially in the hydrolytic action as well as the sulphate itself. These products naturally increase with the concentration of the reacting substances. With a very large increase in the amounts of the bromide and bromate and prolonged boiling, it would be natural to expect the completion of the hydrolysis to the point of liberating bromine equivalent to the entire amount of the acidic ion.

Experimental difficulties, such as the necessity and difficulty of supplying water frequently during the boiling, the periodical titration of the iodine liberated in the receiver, made of doubtful value experiments extended over many hours. When, however, the residue left in the Voit flask in Experiment 7 was treated with a mixture of 1 grm. of potassium iodine and 0·5 grm. of potassium iodate, the iodine set free on boiling for an hour longer indicated that the acidic ion had been very nearly liberated.

The iodine-iodate mixture is extremely sensitive to the action of small amounts of free acid. Experiment showed that the bromide-bromate mixture is also a very delicate indicator of free acid; 0·00018 grm. of sulphuric acid proving to be sufficient to liberate bromine from the bromide-bromate mixture when boiled in the Voit flask under the experimental conditions.

That the progress of the hydrolytic reaction is so much more rapid in the case of the iodide and iodate is apparently due to the specific action of these substances upon the basic aluminium sulphate rather than to a more exact removal of the free acid.

It will be recalled in this connection that, as Moody has shown (*Am. Journ. Sci.*, 1906, xxii., 184), the iodide-iodate mixture, taken in moderate amount, does not further hydrolyse the basic salt produced in the action upon zinc sulphate. A reasonable excess of the bromide-bromate mixture is able in a moderate time to carry the hydrolysis of aluminium sulphate to a fairly definite point corresponding nearly to the removal of five-sixths of the acidic ion, while the iodide-iodate mixture under similar conditions of prolonged action removes practically all the acidic ion.

Some experiments to test the effect of a mixture of potassium chloride and potassium chlorate indicated that the hydrolysis of aluminium sulphate under otherwise similar conditions is very slight compared with that produced by the bromide-bromate mixture or by the iodide-iodate mixture.—*American Journal of Science*, 1907, xxiv., p. 167.

THE PREPARATION OF ACETAMIDE BY THE ACTION OF AMMONIUM HYDROXIDE AND ETHYL ACETATE.

By I. K. and M. A. PHELPS.

It has been stated by Hofmann (*Ber.*, xv., 977) that the action of aqueous ammonia upon ethyl acetate at ordinary temperatures yields after several days' standing considerable amounts of acetamide, but that the amount of acetamide by no means corresponds to the amount of ethyl acetate taken. Hofmann further states that, according to a communication from Dr. Bannow, the yield of acetamide, even when formed in large quantities, is usually not much above 70 per cent of that theoretically demanded. In this same communication Hofmann makes a similar statement in regard to the action of ethyl formate.

In a former paper from the Kent Chemical Laboratory of Yale University (*Am. Journ. Sci.*, xxiv., 173; Chem. News, xcvii., 86) conditions have been shown under which very nearly the theoretical yield of formamide by the action of ammonium hydroxide and ethyl formate is obtained. Now it has been found that conditions closely similar will give theoretical yield as well in the case of ethyl acetate and aqueous ammonia.

For the work given here ethyl acetate of commerce was treated in a separating funnel with sodium carbonate solution, and, after separating from this, was washed with distilled water. The ethyl acetate thus purified from acid

impurities was separated as completely as possible from the water, dried over fused calcium chloride, and then treated again with a fresh portion of fused calcium chloride before fractioning. Portions boiling between 77° and 77·2° were taken as pure ethyl acetate.

Definite portions of the pure ethyl acetate were weighed, and, after chilling below zero in an ice and salt mixture, were mixed in a stoppered reagent bottle with definite volumes of ammonium hydroxide. In some of these experiments the ammonium hydroxide was the pure concentrated ammonium hydroxide of commerce; in others the ammonium hydroxide was made more concentrated by saturating at −10° the pure concentrated ammonium hydroxide of commerce with dry ammonia gas obtained by heating concentrated ammonium hydroxide in a flask connected with a return condenser and drying further the ammonia by passing it through a lime tower; while in a third series of experiments the product obtained by mixing in the cold in a stoppered reagent bottle the ethyl acetate and ammonium hydroxide was saturated in the cold with dry ammonia gas obtained in the manner given above. In every case, after the solution had stood a sufficient time in the reagent bottle stoppered tightly so that the ammonia gas should not escape, it was transferred to a 250 cc. distilling flask, connected with a 100 cc. distilling flask in the usual way for a vacuum distillation, with the use of the least amount of absolute alcohol to rinse the sides of the bottle. The low boiling impurities, ammonia, alcohol, and water, were removed by fractioning *in vacuo* in the usual way, the 250 cc. flask being heated in a bath of hot water finally at 60° for fifteen minutes after the pressure on the manometer registered 15 mm. The acetamide left in the flask was distilled by heating the flask in an acid potassium sulphate bath at 140° to 150°, and was collected in the receiver, cooled by a stream of cold water, and weighed.

No.	Ethyl acetate.	Ammonium hydroxide.		Reaction time.		Acetamide.	
						Theory.	Found.
	Grms.	Cc.	Sp. gr.	Days.	Hrs.	Grms.	Grm.
	A.—*Treatment with* NH_4OH.						
1.	50	50	0·90	3	22	33·57	21·70
2.	50	50	0·90	6	19	33·57	25·60
3.	50	50	0·90	13	—	33·57	29·00
4.	45·4	50	0·90	126	—	30·80	30·36
5.	50	75	0·90	3	23	33·57	26·89
6.	50	75	0·90	6	—	33·57	30·15
7.	50	75	0·90	8	—	33·57	31·18
8.	50	75	0·90	13	—	33·57	34·10
	B.—*Treatment with* NH_4OH *Saturated with* NH_3.						
9.	50	50	—	3	19	33·57	21·03
10.	50	50	—	12	—	33·57	32·80
11.	50	50	—	49	—	33·57	33·12
12.	50	78	—	3	22	33·57	28·81
13.	50	78	—	6	22	33·57	32·53
	C.—*Treatment with* NH_4OH *and Saturation of the Mixture with* NH_3.						
14.	50	50	0·90	3	16	33·57	25·78
15.	50	50	0·90	6	—	33·57	33·71
16.	50	50	0·90	12	6	33·57	33·82
17.	50	50	0·90	20	—	33·57	33·47
18.	50	75	0·90	—	23	33·57	17·72
19.	50	75	0·90	2	—	33·57	30·08
20.	50	75	0·90	3	—	33·57	31·63
21.	50	75	0·90	4	—	33·57	33·62
22.	50	75	0·90	4	6	33·57	34·00

The experiments of Section A are those in which the pure ammonium hydroxide of commerce was used with the ethyl acetate, and after standing suitably the mixtures were distilled *in vacuo* as given above.

The experiments of Section B were conducted in the same way as those in Section A, except that the ammonium hydroxide used was saturated at −10° with dry ammonia before mixing in the cold with the ethyl acetate.

The experiments of Section C were conducted in the same way as those of A, excepting that the entire mass of ethyl acetate and ammonium hydroxide after mixing in the cold was saturated with dry ammonia gas at −8° to −10°.

From an inspection of the results recorded in Section A it is seen that the volume of ammonium hydroxide taken for a given weight of ethyl acetate, as well as the time allowed for the interaction of the ethyl acetate and ammonia, influences the yield of acetamide. The theoretical yield can be obtained with the proportion and concentration of the reagents used here only on long standing. Two weeks' standing at ordinary temperatures with so large an amount as 75 cc. of the ammonium hydroxide for 50 grms. of ethyl acetate will give the yield required by theory, although for smaller proportions of the ammonium hydroxide that time is not sufficient.

It is evident from the results given in Section B that a solution of saturated aqueous ammonia tends to give a larger yield of acetamide in a given time than can be obtained by weaker aqueous ammonia.

In Section C the results show that in shorter time than by the procedure in experiments given in A and B of the table the theoretical yield of acetamide may be obtained by saturating in the cold the mixture of ethyl acetate and ammonium hydroxide, and allowing it to stand either four or six days according to the proportion of the aqueous ammonia present.

It is evident that the time of completion of the reaction is dependent upon the concentration of the ammonia.

It was found that the mixture of ammonium hydroxide and ethyl acetate became homogeneous in the experiments of Section A in about three days, in B in somewhat less time, and twenty-four hours in C. In Experiment 18 the mass became homogeneous at the end of twenty-three hours, and in this single instance distillation was made as soon as this phenomenon appeared. It is evident that the formation of acetamide progresses slowly, and is not at an end as soon as the mass becomes homogeneous.

It was found by experiment that a known weight of pure acetamide treated with 10 cc. of water and fractioned *in vacuo* could be recovered with a loss of less than 0·05 grm. The acetamide tends to hold traces of water; and it was not found possible to remove it by fractional distillation *in vacuo* without danger of loss of very small amounts of acetamide.

The presence and amount of ammonium salt in the acetamide obtained in the procedure outlined above were tested for by the use of a solution of sodium cobalti-nitrite. An experiment showed that 0·0002 grm. of ammonium chloride could be readily detected in the presence of 0·50 grm. of acetamide. The acetamide obtained directly by fractioning *in vacuo* as given above was found to contain traces of ammonia and ammonium salt. In Experiment 8 the crude material was transferred after weighing the product obtained from the vacuum distillation to a watch-glass, and allowed to stand in a desiccator over sulphuric acid for twenty-four hours, and the loss sustained was 0·62 grm., presumably largely water with some ammonia. Some of this loss must have been acetamide also, for by a separate experiment with pure acetamide re-crystallised from benzene it was found that acetamide continually lost in weight in a sulphuric acid desiccator. The acetamide from Experiment 8 after being dried showed the presence of not more than 0·30 grm. of ammonium salt, estimated by the amount of precipitate produced with sodium cobalti-nitrite as compared with the amount of precipitate obtained under similar conditions with ammonium chloride, pure acetamide, and sodium cobalti-nitrite. The material obtained in Experiment 22 was re-distilled with an air condenser under ordinary atmospheric pressure, and yielded 27·5 grms. of product boiling between 221° and 222°. This product showed on testing with sodium cobalti-nitrite no ammonium salt. Theoretically, more ammonium salt might be present in those cases where the standing is

longest. But it was found on re-distillation, under ordinary atmospheric conditions, of the acetamide obtained directly by the processes given above, that ammonium salt was not present in sufficiently large amounts in the different experiments to be noticeable.

It is clear from the work given that acetamide with only traces of impurity may be obtained in quantities barely less than quantitative for the amount of ethyl acetate taken, if ethyl acetate and ammonium hydroxide are mixed in the cold and allowed to stand a suitable length of time. Increasing the amount of ammonium hydroxide employed shortens the time of standing necessary for a theoretical yield, and increasing the concentration of ammonia by saturating the mixture of ethyl acetate and ammonium hydroxide in these proportions with ammonia gas further diminishes, by one-half or more, the time of standing.—*American Journal of Science*, 1907, xxiv., p. 429.

THE DANGER OF OVER SPECIALISATION.*

By L. H. BAEKELAND.

In the ever-recurring discussion of our methods of education and of our pursuits in life, it has been asserted over and over again that "this is the age of specialists."

Is this really so? Does this age create more specialists than former epochs in history? If this be the case, does this tendency keep on increasing, and if so, may it not ultimately impede the higher development of mankind, and reduce us to mere automatic machines?

The political economist tells us that division of labour increases and improves production. We also know that in any pursuit of life specialisation enables us to more thoroughly master the details of a subject.

On the other hand, we ought to admit that even to-day, truly great men, who have achieved distinction by exercising a beneficial influence on the development of our race, were not merely specialists. They were persons of broad general tendencies, although sometimes their superiority was more accidentally manifested in some special line of work. If, to stave this assertion, I started to mention a list of names, I might possibly omit many men of merit known or preferred more particularly by any of you. But I shall take the liberty of turning my argument, by challenging you to name any truly great man who was merely a specialist in one single small branch of human activity.

That one-sided pursuits are apt to make us very narrow-minded will be conceded by many whose misfortune it has been to have to work or live with people who led such a specialised existence. Even the professional fields of specialised activity may lead to short-sighted pettiness. Andrew Carnegie ("The Empire of Business") reinforces my own belief, based on personal experience, when comparing the better class of business men to artists, he wrote:—"I have learned that the artistic career is most narrowing, and produces such petty jealousies, unbounded vanities, and spitefulness, as to furnish me with a great contrast to that which I have found in men of affairs. Music, painting, sculpture, one would think, should prove most powerful in their beneficent effects upon those who labour with them as their daily vocation. Experience, however, is against this."

This apparent shortcoming of artists may be explained by the fact that as a class they are generally very ignorant outside of their own art, which requires more skill than knowledge, and what is worse, to many of them exact knowledge, which might help to broaden their views, is almost repulsive.

But—to come back to first principles—we ought to consider all pursuits of life from a broad general standpoint. I dare say that human life includes, as its noblest attributes, three fundamental tendencies to which all others converge, directly or indirectly. Indeed, nature prompts us—

First, to develop ourselves physically and intellectually—the latter word including all moral development.

Second, to reproduce ourselves, and lend our short existence as individuals for the physical and mental betterment of our race, towards a higher goal of absolute good.

Third, to enjoy life in its material and intellectual comforts as far as the latter contribute directly or indirectly to the two first-named functions. This idea includes naturally the production of wealth and the better use of the same.

Whether we be scientists, philosophers, labourers, artists, merchants, money-lenders, beggars, or thieves, we all obey those laws which predetermine the ultimate destiny of mankind. Whoever, in some way or another, works in harmony with these dictates cannot help being a benefactor to his own race and to himself in particular.

No individual whatever can try to divest himself of any of the above-mentioned attributes or functions of life, without jeopardising in some degree or another the progress of his race.

Let us imagine, for an instant, a society only composed of four distinct classes:—One, wealth-producing but vicious; a second, very moral but inactive; a third, very intelligent but bodily weak; while a fourth class would be composed of physical athletes, very stupid. Fortunately for the welfare of our race, in such a heterogeneous society, free intermarriage would tend to offset the one-sided grouping of these abnormal individuals or specialists—to call them by another name—and would bring about more homogeneity for their descendants. Furthermore, education—the great leveller of one-sided tendencies—would prove another active factor for accomplishing this result. When I speak here of education in its broadest sense, I do not merely limit myself to so-called school education; but I include in this term all influence towards mental development, proceeding from any source whatsoever, as, for instance, self-culture and environment. But, whenever education tends to develop one of our faculties beyond reasonable necessity and to the detriment of other functions, we drift towards mental deformity—a freak; and this in about the same manner as a particular muscle exercised beyond normal requirements will leave the remainder of the body insufficiently developed and out of harmony with the other anatomical parts.

Many fundamental errors have been committed by such men as spoke or wrote of the culture or the civilisation of a given nation, without according full importance to above considerations. Moreover, history teaches us that a one-sided or specialised education has been the defect of nations of the past, even to a greater extent than it occurs in our present civilisation. Many examples can we give to show that such a one-sided culture was largely to blame for the downfall of at one time powerful races. The Greeks, in their over specialisation of art, neglected beyond measure the study of nature. Had her philosophers steadied their thoughts by giving more attention to the careful observation of natural phenomena, instead of dreamingly searching a solution for all problems by analytical reasoning, they would not have been led astray into casuistry and sophistry and scepticism. The great laws of nature might have opened their minds to a better understanding of equity and rights of man; while now history has to record that even the most progressive and radical Greek philosophers proclaimed chattel slavery as an indispensable institution of society. In the same way, a large part of their literature was devoted to beautifully sounding, well-polished sentences, dealing mostly with imagination. The Greek writers, in their search for effect, gave their fancy full play whenever they described the war exploits of their heroes, with the result that they put themselves on record in history as the biggest braggarts in prose and in rhyme.

* Read before the New York Section of the American Chemical Society. From *Science*, 1907, xxv., No. 648.

As another example of one-sided culture let me remind you of the inhabitants of India, who became overawed by the conception of the immensity of the universe, and the relative insignificant smallness of man. Exaggerating this feeling, they too failed to grasp the full meaning of harmony in nature, and so neglected to give sufficient attention to the material development of their race. This doomed to stagnation an otherwise very intellectual people; it rendered possible their subjugation under the strong and forceful arm of warlike tribes, morally less developed, but physically better adapted for the perpetuation and multiplication of their sturdier race.

In the same way, the Roman Empire fell as a result of the wilful ignorance of the true principles of equity; her poorer classes, or vanquished foes, were denied their natural rights by their aristocratic masters. This heterogeneity of the people led to all the excesses which brought about the fall of what once had been a mighty empire.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Annual General Meeting, February 14th, 1908.

Prof. J. Perry, F.R.S., President, in the Chair.

The Secretary read the report of the Council for the past year:—

Since the last Annual General Meeting, thirteen ordinary science meetings and one informal meeting of the Society have been held. Of these twelve were held at the Royal College of Science; one, that on June 14th, was held at University College, by invitation of Prof. J. A. Fleming, F.R.S.; and one, that on June 28th, at the Central Technical College, by invitation of Prof. W. E. Ayrton, F.R.S. The average attendance at the meetings has been 58 as compared with 50 during the preceding year.

The third Annual Exhibition of Apparatus by manufacturers was held on December 13th, when the attendance of Fellows and visitors amounted to about 200.

Light refreshments are now provided before the afternoon meetings and after the evening meetings. This innovation appears to be appreciated, and it is hoped that the opportunity thus afforded will enable Fellows to become personally acquainted with each other, and to interchange opinions more readily than has been possible hitherto.

The number of ordinary Fellows now on the roll, as distinct from Honorary Fellows, is 437, an increase of 11 on the number last year; 27 new Fellows have been elected, two Fellows have been reinstated, and two Honorary Fellows, namely, Prof. Gabriel Lippmann and Prof. Simon Newcomb, have been elected. There have been 11 resignations, the names of two Fellows have been struck off the list for non-payment of subscriptions; and the Society has to mourn the loss by death of 6 Fellows, namely, one Honorary Fellow, P. J. C. Jules Janssen, and 5 Ordinary Fellows, namely, Lord Kelvin, Sir W. Perkin, J. R. Brittle, J. MacFarlane Gray, and J. W. Kearton.

The report was adopted.

The Treasurer read his report for the year 1907:—

The position of the Society this year shows a decided improvement. There are more new members than usual, and subscriptions have been paid more punctually. The balance in bank has increased by nearly £240, more than £100 of which, however, is due to composition-fees and recovered income tax. The value of the securities has declined somewhat owing to the general depression, but this is probably of a temporary nature. There are no outstanding liabilities, and the income shows a healthy tendency to exceed the expenditure.

The report was adopted.

The following Officers and Council were elected for the ensuing year:—

President—C. Chree, Sc.D., F.R.S.

Vice-Presidents—Those who have filled the Office of President, together with W. Duddell, F.R.S.; H. M. Elder, M.A.; Prof. J. A. Ewing, F.R.S.; and W. Watson, D.Sc., F.R.S.

Secretaries—W. R. Cooper, M.A., and Prof. W. Cassie, M.A.

Foreign Secretary—Prof. S. P. Thompson, D.Sc., F.R.S,

Treasurer—Prof. H. L. Callendar, M.A., F.R.S.

Librarian—W. Watson, D.Sc., F.R.S.

Other Members of Council—A. Campbell, B.A.; W. H. Eccles, D.Sc.; A. Griffiths, D.Sc.; J. A. Harker, D.Sc.; Prof. C. H. Lees, D.Sc., F.R.S.; T. Mather, F.R.S.; A. Russell, M.A.; S. Skinner, M.A.; S. W. J. Smith, M.A., Prof. L. R. Wilberforce, M.A.

Dr. Chree then took the Chair and delivered an Address.

The Address mentioned that whilst the losses of the Society during the past year had been few, they included two most distinguished Fellows—Lord Kelvin and Sir W. H. Perkin, who both joined the Society in 1875. It was hardly the place to refer to Perkin's work, as it was his discoveries in chemistry that had brought him distinction. Lord Kelvin had been one of the earliest Presidents of the Society. During his lifetime British physicists had the satisfaction of feeling assured that their number included the man who was universally recognised as the foremost in their branch of knowledge. There had already appeared obituary notices of Lord Kelvin by old pupils and others who knew him intimately. The account by Prof. Ayrton in *The Times* gave a particularly life-like portrait. Lord Kelvin was active in a great variety of fields, his work appealing to very different types of mind. The fact that he an eminent pure scientist, was the inventor of many instruments of high practical utility, had done a great deal to impress the average Englishman with a sense of the value of science. Another side of Lord Kelvin's activity, his speculations as to matters such as the age or internal state of the earth, appealed strongly to the popular imagination. But apart from what appealed directly to the public Lord Kelvin's writings contained a vast amount of what was at once solid and highly original. He had made contributions of high value to hydrodynamics, heat, elasticity, magnetism, electricity, and optical theory.

Whilst an able analyst, Lord Kelvin seemed to take comparatively little interest in analysis for its own sake. His interest seemed always to centre in the physical result which the analysis enabled him to reach. He had such a constant flow of new ideas that it was repugnant to him to spend time in perfecting or extending analysis more than was immediately necessary at the time. One very pleasing feature in Lord Kelvin's character was his generosity in recognising the work of younger and unknown men.

Passing to the question of the progress of the Society, the speaker said that during the last five years the membership had increased by about 7 per cent. With the increased number of persons concerned with science, an increase of membership seemed a natural consequence, but it should be remembered that with the continual increase of specialisation new societies tended to arise. Considering modern tendencies, it was perhaps a little strange that so few ladies had availed themselves of the fact that they were eligible to the Fellowship of the Society.

The speaker referred to the fact that tea and light refreshments were now provided at the meetings, and hoped the departure would be generally appreciated. Referring to a resolution of the Council inviting readers of papers and others to be considerate in their demands on time when addressing the Society, the speaker expressed a hope that Fellows would not be found lacking in reasonableness. When several papers were down for reading, it was clearly

impossible for all the authors to go into minute details without exhausting the patience of the meeting. In general, what was most appropriate was a summary intelligible to those who were not specialists in the particular subject of the paper.

The speaker than proceeded to refer to the magnetic results obtained by the National Antarctic Expedition of 1901-4. The expedition had been furnished with magnetographs, and the reduction and discussion of the curves had been entrusted to the National Physical Laboratory. Thanks to the acquiescence of the Officials of the Royal Society and the Director of the National Physical Laboratory, he was able to give a general preliminary account of some of the results, a full discussion of which would appear in the official publications of the Expedition. Before entering on a description of the results, he spoke of the nature of the preparations that should in his opinion be made in the case of any future National Scientific Expedition. It was most important that the observers should have a special preliminary training lasting over a good many months, and should be practised in the use of the instruments they would have to employ in the course of the expedition. These instruments ought thus to be ready for use and fully tested months before the date when the expedition was to set out.

A programme, based at once on special scientific knowledge and on common sense, should be got out in good time, so as to admit of sufficient rehearsals by the observers prior to their departure. A form of judicial inquiry after the return of the expedition into the value of the results obtained might be useful in securing that meritorious scientific work would not be overlooked, as compared to what appealed more directly to the popular imagination.

After paying a tribute to the assistance he had received from Mr. Bernacchi, the Physicist of the National Antarctic Expedition, and from members of the staff of the National Physical Laboratory, the speaker exhibited and described a number of lantern-slides relating mainly to the diurnal inequalities of the magnetic elements in the Antarctic. A few slides of corresponding Kew results were shown for intercomparison. Comparing slides of actual records taken at Kew and in the Antarctic, the speaker dwelt on the relatively highly disturbed nature of the latter. In the Antarctic, the declination and horizontal force magnets were practically never at rest. So large and incessant were the disturbances, that no idea of the nature of the regular diurnal inequality was obtainable from mere inspection of individual curves. Diurnal inequalities, however, derived from the curves of single months, and still more those derived from the curves of a whole season of the year, proved to be of a comparatively smooth character. Slides were exhibited showing the nature of these inequalities for the several elements.

CORRESPONDENCE.

COPPER AND BRASS INSTITUTE.

To the Editor of the Chemical News.

Sir,—A meeting of copper and brass manufacturers, engineers, and others, was held in Manchester on February 13th, 1908. Mr. W. H. Johnson (Messrs. Richard Johnson, Clapham, and Morris, Ltd., Manchester) was elected to the Chair.

It was unanimously resolved to form a Copper and Brass Institute.

The impetus to this movement was given by a letter from Mr. W. H. A. Robertson, of Bedford, which appeared in several papers on January 24th.

The objects of the Institute are similar to those of the well-known Iron and Steel Institute, viz.:—

1. To afford a means of communication between members of the trades in question, bearing upon their respective manufactures, excluding all questions connected with wages and trade regulation.
2. To arrange periodical meetings for the purpose of discussing practical and scientific subjects relating to the manufacture, working up, and use of the non-ferrous metals.

It is not the intention of the founders to limit the Institute to the copper and brass trades, but to include all those connected with the commercially important non-ferrous metals and their alloys, such as lead, zinc, tin, aluminium, nickel, silver, gold, platinum, &c., and their alloys.

In order to obtain a much wider and fuller discussion than was possible at the preliminary meeting, and to define the constitution and method of procedure of the Institute, it is proposed to hold a meeting in the Midland Hotel, Manchester, on Tuesday, March 10th, at 4 p.m., to which all those interested are most cordially invited. This letter is the only public summons to the meeting that will be issued.

All who hope to attend the meeting or take an interest in the formation of the proposed Institute, are requested to send their names to any of the following:—

William H. Johnson, care of Rd. Johnson, Clapham, and Morris, Ltd., Manchester.
H. C. H. Carpenter, Professor of Metallurgy, The University, Manchester.
G. G. Poppleton, care of The Wholesale Traders' Association for the Hardware and Metal Industries, Birmingham.

Manchester, February 17th, 1908.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Biological Chemistry Examination.—(Reply to P.).—If P. will call at the Institute, I shall be pleased to show him the books in the Library which would assist him in preparing for the Examination.—R. B. Pilcher, Registrar.

MEETINGS FOR THE WEEK.

Monday, March 2nd.—Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "Considerations affecting the 'Strength' of Wheat Flours," by J. L. Baker and H. F. E. Hulton.
Tuesday, 3rd.—Royal Institution, 3. "Membranes—Their Structure, Uses, and Products," by Prof. William Stirling, M.A., LL.D., D.Sc., &c.
Wednesday, 4th.—Royal Society of Arts, 8. "Modern Dairy Practice," by L. M. Douglas.
Thursday, 5th.—Royal Institution, 3. "Early British History and Epigraphy," by Prof. Sir John Rhys, M.A., &c.
—— Chemical, 8.30. "Solubility of Iodine in Water," by H. Hartley and N. P. Campbell. "Traces of a New Tin Group Element in Thorianite," by Miss C. de B. Evans.
Friday, 6th.—Royal Institution, 9. "Recent Earthquakes," by Prof. John Milne, F.R.S., &c.
Saturday, 7th.—Royal Institution, 3. "Electric Discharges through Gases," by Prof. J. J. Thomson, F.R.S.

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THE CHEMICAL NEWS.

Vol. XCVII., No. 2519.

ON THE

PHYSICAL ASPECT OF THE ATOMIC THEORY.*

By Prof. J. LARMOR, Sec.R.S.

The lecture began by setting out a physical reason *à priori* why matter should be constituted of discrete particles instead of being continuous. The requirements of physics demand an ether to serve as the means of communication between portions of matter out of contact with each other; and space can hardly be conceived as *fully* occupied simultaneously by two media, matter and ether; hence the matter must be constituted of discrete centres or nuclei, determining permanent collocations of energy in the ether, which are, in fact, primordial atoms and their fields of force. The feasible problem of atomic physics is to build up an adequate idea of the dynamic constitution of these ethereal fields of force; there is the problem beyond, to determine the intrinsic constitution of the central nuclei to which they are attached, which may remain permanently beyond our ken. The expansion of our ideas about the atoms and their structural connection with the ether was traced from their origin in Descartes, through Huygens and Newton down to the more definite modern types of representation, as regards various essential features that are afforded by the vortex atom and the electron.

In the hands of the physicists, especially Newton and Young, the atom had already become a complex structure capable of definite inherent periods of free vibration, but so far as physics was concerned the same substance might include various kinds of atoms. The fundamental advance of Dalton, which assured an adequate domain to chemistry as an exact science, was the proof that each compound substance is definite as regards its molecule, and that all atoms of the same elementary body are identical. Whether this absolute identity points to the atom of each chemical element being a dynamically balanced structure of primordial atoms, one of a limited number of possible definite types of structure—which would be a perfectly reasonable way of accounting for this remarkable identity—remains an open question. The periodic relations of the elements, connected most closely with the name of Mendeleeff, certainly indicate that, whatever may be the case as regards the kernel, the outer structure of the atom, so to speak, which is the link through the ether between the nucleus and the outside world, is constituted on the basis of a common ultimate element which may be the electron.

The remark of Maxwell seems still to retain its force, that the mechanism of biological evolution could hardly reside in atoms, primordial or other, which had not much vaster underlying complication than is needed for their purely physical relations. The facts of biology may possibly demand a hypothesis such as the above, that atoms not in intimate contact interact through the ether according to general physical laws in the manner required to constitute the physical cosmos; but that there may also be a closer inter-penetration of atomic nuclei in which far more complex agencies are involved.

The mechanical atom of the earlier physicists, considered in this physical aspect as an unknown core determining the field of activity in the surrounding ether, has had, since Faraday's discoveries in electrolysis, to take on a more definite form as the electrical atom. The result had been fully reached by Faraday himself, though it needed to be enforced later by Helmholtz, that the energies which have play in chemical combination are of electrical origin, implying thereby, according to Maxwell's interpretation, energies of intrinsic stress and motion brought to bear from atomic stores located in the adjacent ether. This doctrine has led on to the modern theory of purely electric atoms which was already demonstrable on theoretical grounds, of course in a way less definite than we now know it, before the very remarkable discovery of electrons actually free had been reached, through the phenomena of radio-activity either electrically induced or spontaneous. Here, again, there is the same choice of points of view open to tentative development. We may proceed on a limited hypothesis as if the electrons are the sole primordial atoms; or we may assume that there are various ultimate atoms which have existence and structure of their own, of type largely unknown and independent of the ether, and that the electrons which are associated with them, whether temporarily or intrinsically, form merely one feature of their constitution, viz., their means of communication with the ether, and through it with other atoms at a distance to form an ordered universe.

In any case we are right in following out the hypothesis, there being, in fact, none other open to us, that the purely physical manifestations of atoms—those, namely, that, owing to the simple inter-connection involved in their common seat in the ether, aggregate into the definite physical qualities of matter in bulk—are in the main or in most circumstances practically a group by themselves, and that they are thus capable of being investigated on these broad simple principles of dynamics, which Newton definitely formulated as a suitable foundation for the analysis of general physical activity as it presents itself in the universe. This so-called mechanical hypothesis has been eminently the fruitful one; it pointed the way to the principle of the conservation of energy, and is now elucidating the wider principle of its definitely limited availability; it gave a rational explanation of the spectrum and of radiation in general, which has proved a reliable and precise guide to investigation of phenomena far below the surface, such as the selective dispersion of light and the magnetic action on radiation; it reduced electrical phenomena to order and control, and connected them with light. It must therefore be presumed to be available as the clue for the further elucidation of pressing problems, such as the nature of the transmission of gravitation and of the intimate operation of chemical affinities.

The tendency to reject dynamical analysis as artificial in such subjects as electro-dynamics, which received some stimulus from the theoretical writings of Hertz, seems to overlook the fact that it was precisely as a compact working basis suitable for the formulation of experience in its more general aspects, that the Newtonian scheme of dynamics was put forward by its author. In the course of time that scheme has become wider and more elastic, through the generalisations of Lagrange and Hamilton, expounded forcibly on the physical side by Kelvin, Helmholtz, and various others. But to take over the final results, and dress them in new language devoid of the dynamical implication, seems to involve a misreading of scientific evolution.

This position may be enforced by a quotation from the final exposition of Newton's views on the scope of Natural Philosophy in general, inserted by himself at the end of the famous "Queries" ("Opticks," Ed. 3, p. 377):—"To tell us that every Species of Things is endow'd with an occult specifick Quality by which it acts and produces manifest Effects is to tell us nothing. But to derive two or three general Principles of Motion from Phænomena, and afterwards to tell us how the Properties and Actions of all corporeal Things follow from those manifest Principles, would be a very great step in Philosophy, though the Causes of those Principles were not yet discovered. And therefore I scruple not to propose the Principles of Motion above mention'd, they being of very general Extent, and leave their Causes to be found out." Then he proceeds to associate his Laws of Motion with an atomic theory.

* Abstract of the Wilde Lecture delivered before the Manchester Literary and Philosophical Society, March 3, 1908.

A review of the electrical side of the atomic theory requires a consideration of the phenomena of ionisation in solutions. The theoretical difficulties which have presented themselves in this subject were discussed, in particular the nature of the energy changes which must occur when a salt is dissolved, and thus split into separate ions. Reasoning from the processes of the voltaic cell, as expounded after Faraday by Helmholtz, the view is advanced that an equivalent of purely local potential energy of affinity with the solvent must be exhausted in order to provide for the separation of the ions, but without much violent motional disturbance such as would diffuse partially away into the form of heat. This absence of such motional dissipation of the energies of affinity, as indicated, for example, by their almost complete mechanical availability in a Daniells cell, is perhaps connected with the intimate contacts in confined spaces which are characteristic of the processes at the electrodes by which the chemical change is effected. It is suggested that a similar mode of explanation applies to the very high, sometimes nearly complete, mechanical availability (Berthelot) of the energy of chemical transformations in dense media such as liquids and solids, as contrasted with dilute systems such as gases, which the recent work of Nernst and his pupils has brought again to the front.

The lecture passes on to touch on those extensive branches of chemical physics to which the constitution of the atom is not essential, where only a statistical grasp of the molecular associations and dissociations that are taking place is required. The quantitative theory of chemical equilibrium and of progress of chemical change, as regards dilute systems, comes under this head, of which the prototype and the most highly developed example is the kinetic theory of gases. The modern theory of electrodynamics as based on the displacements and motions of electrons is in the main analogous; and the theory of gravitation, when it comes to light, will be of the same kind.

In particular the molecular aspect of reaction in gases is passed under review. Reasons are brought forward for holding that in gases all ultimate reactions are of necessity mono- or bimolecular. If this be so, the important work now proceeding with regard to the effect of impurities in promoting or inhibiting gaseous reactions, must lead to fuller knowledge of the transient molecules or radicles which are formed in the destructive encounter of a pair of the reacting molecules, and are the carriers or intermediaries leading finally to poly-molecular change; while the same transient combinations may be approachable independently from another side as affording the interpretation of the complex banded spectra of emission or absorption in gaseous media.

The very remarkable and most fruitful and prophetic symbolic theories of molecular structure, especially for the complex molecules of organic chemistry, have not yet proved capable of dynamical interpretation; it seems necessary, however, to admit on account of the wide range of physical properties that are nearly atomically additive that stereochemical collocations do represent in some real way the actual aggregation of the atoms instead of mere symbolical representation of it. Recent investigation appears to bring out in certain cases a somewhat definite relation between the configuration of the molecule and the crystalline form of its physical aggregations, which, though reasonable, could not have been foreseen *à priori*; exact crystallographic measurements may thus in time afford another intimate clue to the molecular structures in related series of compounds.

Royal Institution.—Professor Milne will be unable to deliver his Discourse at the Royal Institution on "Recent Earthquakes" on Friday, the 6th instant. The Discourse on that date will be delivered by Professor Love on "The Figure and Constitution of the Earth." Professor Milne's Discourse is postponed until March 20.

ESTIMATION OF COCOANUT OIL IN BUTTER.

By RAYMOND ROSS, F.I.C., and JOSEPH RACE, A.I.C.

In reference to the papers by Mr. T. R. Hodgson which recently appeared in the Chemical News (vol. xcvi., pp. 273, 288, 297), on the estimation of cocoanut oil in butter by means of $KMnO_4$, we should like to point out that the process as devised by him is in our opinion unworkable.

The process essentially consists of the oxidation of 20 cc. of a 0·1 per cent solution of the saponified fat by means of 50 cc. of decinormal $KMnO_4$ and 50 cc. of H_2SO_4 (50 per cent). The mixture is heated on the water-bath for at least half-an-hour, and subsequently titrated with standard oxalic acid or ferrous ammonium sulphate. The author recommends the use of the latter.

Firstly, we should like to point out that H_2SO_4 of the strength prescribed exerts under the conditions laid down a considerable action on $KMnO_4$. Thus, on treating 20 cc. of water and 50 cc. of decinormal $KMnO_4$ on the water-bath for thirty-five minutes with varying amounts of 50 per cent H_2SO_4, the following results were obtained:—

20 cc. of water + 50 cc. of decinormal $KMnO_4$—	Cc. of decinormal oxalic acid required.
+ 5 cc. H_2SO_4 (50 per cent)	48·0
+ 10 ,, ,,	42·5
+ 15 ,, ,,	31·0
+ 25 ,, ,,	22·4
+ 40 ,, ,,	18·5
+ 50 ,, ,,	13·7

From these results it is evident that the quantity of $KMnO_4$ remaining depends largely upon the amount of acid present. If, however, only small quantities of H_2SO_4 are used, concordant results can be obtained, and we therefore tried Mr. Hodgson's process using only 5 cc. of 50 per cent acid. Two samples of butter and two of cocoanut oil treated in this manner gave the following oxygen equivalents:—

	Oxygen equivalent.
Butter No. 1	60·0
Butter No. 2	62·3
Cocoanut oil No. 1	54·7
Cocoanut oil No. 2	57·6

Butter No. 2 was farmer's butter of known origin and purity. These results being unsatisfactory from the point of view of differentiation we varied the process by effecting the oxidation in alkaline solution, as by this means we thought that the two fats might vary in their oxygen equivalents owing to the formation of varying amounts of hydroxy acids. That this was not the case is shown by the following figures:—

	Oxygen equivalent.
Butter No. 2	57·3
Cocoanut oil	49·1

We thought, however, that it might be of interest to know to what extent oxidation took place with various fats and fatty acids when treated with $KMnO_4$ in slightly acid solution without previous saponification. The following table gives the results obtained by oxidation of small quantities of the substance with a large excess of permanganate and 5 cc. of 50 per cent acid.

Substance.	Oxygen equivalent.
Butter	2·9
Butter fatty acids	3·6
Cocoanut oil	1·8
Cocoanut oil fatty acids	0·8
Palm oil fatty acids	19·8
Lactic acid	20·7
Acetic acid	4·5
Oleic acid	15·4
Stearic acid	3·3
Glycerol	116·0

Further, working as before but in alkaline solution, after saponification we obtained the following figures:—

Substance.	Oxygen equivalent.
Butter fatty acids	48·0
Cocoanut oil fatty acids	43·0
Cotton-seed oil fatty acids	46·7
Lactic acid	37·6
Oleic acid	55·3
Stearic acid	14·7
Cotton-seed oil	75·3

From the above results it is clear that as a means of detecting adulteration the process is quite useless.

It will be observed that there is a great difference in the oxygen equivalents of saponified and unsaponified fats, and that this difference also extends to the fatty acids is shown by the following:—

Oxidation in Acid Solution with previous Saponification.

Substance.	Oxygen equivalent.
Butter fatty acids	45·6
Cocoanut oil fatty acids	40·1
Cotton-seed oil fatty acids	43·8

It is therefore evident that after saponification considerably higher results are obtained than with untreated fats and fatty acids. The reason for this is probably that when the soap solution is decomposed by acid, the fatty acids are suspended in the liquid in a very fine state of division. If this were the case it might be expected that the more concentrated the soap solution the lower would be the oxygen equivalents obtained. This deduction is supported by the figures given below, which were obtained by oxidation of varying quantities of butter-fat in alkaline solution, the titration being made immediately after slight acidification.

Weight of butter-fat used.	Oxygen equivalent.
0·015	88·0
0·045	56·9
0·090	48·9

The difference in the oxygen equivalents of the fats and their fatty acids must be due to the glycerol and the soluble fatty acids. As both butter and cocoanut oil contain approximately equal quantities (10 per cent) of glycerol, which has an oxygen equivalent of about 122·0 in acid solution, it is evident that the glycerol present can only account for a difference of 12 in the oxygen equivalent, assuming that none of it is lost during the evaporation of the alcoholic soap solution. It therefore follows that the soluble fatty acids, which are only present in very small quantities, must have a considerable oxygen equivalent.

Lastly, we should like to call attention to the difficulty experienced in obtaining a good end reaction owing to the retention of the hydrated oxides of Mn by the insoluble fatty acids liberated on the addition of acid. This is the case with both oxalic acid and ferrous ammonium sulphate, but in the latter case there is the additional difficulty of the yellow colour due to the oxidised iron salt. It is possible that the addition of phosphoric acid might overcome this difficulty.

ON THE VOLUMETRIC ESTIMATION OF LANTHANUM AS THE OXALATE.

By W. A. DRUSHEL.

Nearly thirty years ago Stolba stated that cerium, lanthanum, and didymium may be estimated by treating their oxalates with potassium permanganate in the presence of sulphuric acid, but gave no experimental evidence in the form of analytical results (*Sitzber. d. Böhm. Gesell. d. Wissenschaften*, iv., July, 1879; *Zeit. Anal. Chem.*, xix., 194). Later this statement of Stolba was confirmed by a paper from the Kent Chemical Laboratory of Yale University (Browning, *Am. Journ. Sci.*, 1899, viii., 451), in which it was shown that cerium may be estimated by precipitating cerium oxalate with a definite amount of a standard solution of ammonium oxalate used in excess. The precipitated cerium oxalate was decomposed by dilute sulphuric acid, and the oxalate estimated by permanganate, and the ammonium oxalate in excess of the amount required for the precipitation was also estimated by permanganate. By this process the results were checked.

The work to be described was undertaken to determine the best conditions for the estimation of lanthanum as the oxalate, and also to furnish the desirable experimental data in support of Stolba's original statement.

For this work about 10 grms. of pure ammonium lanthanum nitrate were prepared by separating the lanthanum and didymium from the cerium in a kilogrm. of the mixed sulphates by Mosander's chlorine method. The mixture of lanthanum and didymium chlorides thus obtained, having been shown to be free from cerium by the hydrogen peroxide test, was converted into a mixture of ammonium lanthanum nitrate and ammonium didymium nitrate. By fifty re-crystallisations about 40 grms. of pure ammonium lanthanum nitrate were obtained. This salt was dissolved in 80 cc. of water, and the solution through a depth of 19 cc. showed no trace of absorption bands. A few cc. of the solution evaporated to dryness and ignited gave a pure white oxide. Out of this solution of the double nitrate about 10 grms. were re-crystallised for the experimental work of this paper. The procedure is as follows:—

From a neutral lanthanum solution (a 1 per cent ammonium lanthanum nitrate solution being used in this work) the oxalate is precipitated by a measured amount of standard *n*/10 oxalic acid, or ammonium oxalate after the addition of a few drops of acetic acid. The precipitate is thoroughly stirred and allowed to settle. It is then filtered through a perforated crucible fitted with an asbestos felt. After thoroughly washing with water the crucible and precipitate are placed in a beaker with 100 to 300 cc. of water and 10 to 30 cc. of (1:4) sulphuric acid. The contents of the beaker are heated nearly to boiling, and at once titrated to colour with standard potassium permanganate. The filtrate is similarly titrated as a check on the titration of the precipitate. The lanthanum is calculated as La_2O_3 from the two titrations. The mean of the two closely agreeing values thus obtained is taken.

The solution of ammonium lanthanum nitrate used in this work was standardised by evaporating measured portions to dryness, and carefully igniting the residue to constant weight.

Table of Results.

(Lanthanum .. .. 138·9)

	La_2O_3 taken as the double nitrate.	La_2O_3 found.		Average.	Error.
		Precipitate.	Filtrate.		
	Grm.	Grm.	Grm.	Grm.	Grm.
1.	0·0148	0·0152	0·0144	0·0148	0·0000
2.	0·0148	0·0149	0·0139	0·0144	−0·0004
3.	0·0296	0·0302	0·0291	0·0296	0·0000
4.	0·0296	0·0302	0·0293	0·0297	+0·0001
5.	0·0592	0·0599	0·0586	0·0593	+0·0001
6.	0·0592	0·0598	0·0585	0·0592	0·0000
7.	0·1184	0·1191	0·1179	0·1185	+0·0001
8.	0·1184	0·1191	0·1182	0·1187	+0·0003
9.	0·2368	0·2376	0·2362	0·2369	+0·0001
10.	0·0148	0·0149	0·0145	0·0147	−0·0001
11.	0·0148	0·0150	0·0147	0·0148	0·0000
12.	0·0296	0·0298	0·0293	0·0295	−0·0001
13.	0·0592	0·0596	0·0589	0·0593	+0·0001
14.	0·1184	0·1190	0·1182	0·1186	+0·0002
15.	0·1036	0·1040	0·1029	0·1035	−0·0001

In Experiments 1 to 9 ammonium oxalate was used in making the precipitation, in 10 to 15 oxalic acid was used.

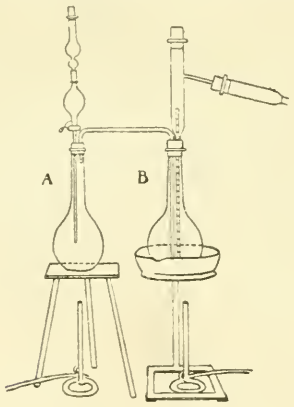
In conclusion, the author acknowledges his indebtedness to Prof. Philip E. Browning for helpful suggestions during the progress of the work.—*American Journal of Science*, xxiv., p. 197.

THE USE OF ZINC CHLORIDE IN THE ESTERIFICATION OF SUCCINIC ACID.

By I. K. and M. A. PHELPS.

IN a former paper from the Kent Chemical Laboratory of Yale University (*Am. Journ. Sci.*, xxxiii., 368) it has been shown that in the action of succinic acid with ethyl alcohol containing hydrochloric acid to form diethyl succinic ester, the largest yield from a known weight of succinic acid is obtained where maximum dehydration is accomplished. In the work given here the action of zinc chloride in forming diethyl succinic ester in the mixture of succinic acid and ethyl alcohol both with and without the addition of hydrochloric acid is shown.

The apparatus figured was used in all of the experiments recorded here. Two round bottom flasks of 500 cc. capacity, each provided with inlet and outlet tubes held in rubber stoppers, were connected as shown. Of these, B, connected to a condenser through a Hempel column carried a thermometer, and from flask A an inlet tube adjusted to dip beneath the liquid to the same depth as the thermometer. The flask A carried a separating funnel provided with a drying tube, as well as the exit tube to the flask B. In the flask B succinic acid was heated, by means of a bath of acid potassium sulphate, in some experiments with a definite amount of absolute alcohol alone, in others with the same amount of absolute alcohol containing hydrochloric acid gas, while from the flask A gaseous alcohol in most cases, and in a few cases gaseous alcohol with hydrochloric acid, was driven over into the mixture in B where esterification took place. The crude succinic ester



left in flask B was freed from impurities by treating with sodium carbonate solution after first removing the zinc chloride by washing with water. The ester was freed from carbonate by rinsing with distilled water containing sodium chloride. The mass of ester carried mechanically with the several wash-waters was extracted by shaking out separately three times with ether. The ether extracts and the succinic ester were gathered in a 250 cc. distilling flask fitted in the usual way for a vacuum distillation with a 100 cc. distilling flask used as a receiver, and, after fractioning off low boiling impurities, largely ether, alcohol, and water, was distilled and collected in the receiver, cooled by a stream of water striking it constantly, and then weighed.

The pure zinc chloride of commerce was freshly fused for use in the experiments. The alcohol employed was made as anhydrous as can be obtained by successive treatments with fresh quicklime. The alcohol containing hydrochloric acid was charged with the dry gas in the proportion of 10 grms. to the litre. The succinic acid used was in most cases the pure acid of commerce, in the others pure succinic acid made by re-crystallising the product formed by the hydrolysis of the pure ester in the presence of nitric acid.

The result obtained in Experiment 1 of the table was found by heating with an acid potassium sulphate bath in the flask B a known weight of succinic acid with 40 cc. of the total amount of absolute alcohol used in presence of 10 grms. of zinc chloride at a temperature of 100—110°, while driving into it the remainder of the alcohol in the form of vapour from flask A. All vapours from the flask passed through the Hempel column to the condenser. The Hempel column had an active surface of beads of 10 cm. in height and a diameter of 2 cm. At its lower end it was in connection with a tube 5 cm. in length and of 0·5 cm. bore, and had an opening blown in its side 1·5 cm. from the end. By the use of a column of this construction the hot vapour is enabled to go upward while the condensed liquid flows downward readily. It was found that by the use of this column neither succinic ester nor succinic acid distilled in such amount, if at all, that it could be detected in the liquid distillate. The impure ester in flask B, when all alcohol as vapour from flask A had been passed into it, was cooled, and then poured into a separating funnel containing water with ice, using a small amount of ether to rinse the ester from the flask, and the zinc chloride was removed as far as possible. After separating the ester from this solution any acid impurities were neutralised with an excess of sodium carbonate in solution, and the ethereal solution was then washed with distilled water. The aqueous solutions in which the ester had been washed were shaken out three times separately with ether. The ethereal extracts were gathered in a 250 cc. distilling flask connected in the usual way for a vacuum distillation with a 100 cc. distilling flask used as a receiver. The low boiling impurities, ether, alcohol and water largely, were separated by a vacuum fractionation, the 250 cc. flask being heated in a bath of hot water at 60° finally for fifteen minutes after the manometer registered 15 mm., and the succinic ester was then distilled and weighed.

The procedure in case of Experiments 2 and 3 was the same excepting that the alcohol used was charged with hydrochloric acid in the proportion of 10 grms. to the litre; and in case of No. 3, and, also, in case of all other experiments in the table where only 1 grm. of zinc chloride was used, the rinsing with cold water before neutralising with sodium carbonate was omitted. In Experiments 4 to 10 the 40 cc. of alcohol heated with the succinic acid contained 1·25 per cent of hydrochloric acid gas, while absolute alcohol in amounts recorded in the table distilled into this mixture heated at 100—110°.

No.	Succinic acid.	$ZnCl_2$.	Alcohol with HCl.		Reaction time.		Succinic ester.		
							Theory.	Found.	Per cent.
	Grms.	Grms.	Cc.	Per cent.	Hrs.	Mins.	Grms.	Grms.	
1.	50	10	200	0	2	30	73·7	66·90	90·8
2.	50	10	200	1·25	0	50	73·7	71·25	96·7
3.	50	1	200	1·25	0	45	73·7	69·40	94·2
			160	0					
4.	50	10	40	1·25	4	0	73·7	69·70	94·6
			160	0					
5.	50	10	40	1·25	0	45	73·7	72·00	97·7
			60	0					
6.	50	1	40	1·25	0	20	73·7	53·15	72·1
			60	0					
7.	50	1	40	1·25	0	55	73·7	52·05	70·6
			160	0					
8.	50	1	40	1·25	1	0	73·7	70·30	95·4
			160	0					
9.	50	1	40	1·25	0	45	73·7	71·78	97·4
			160	0					
10.	50	1	40	1·25	0	50	73·7	71·88	97·5

From an inspection of the results in the table, it is evident that in presence of zinc chloride to the amount of 10 grms. with the proportions of succinic acid and alcohol given in the table, a fair yield of succinic ester is possible. Introducing hydrochloric acid and shortening the time of the

reaction tends to increase the yield as shown by Experiment 2. Reducing the amount of zinc chloride present gives satisfactory results, as is clear by comparing Experiment 5 with 9 and 10. Although the amount of alcohol present in 6 and 7 during the reaction is double that theoretically required to esterify the acid present, it is not sufficient for the esterification under the conditions of the experiments. The simplest conditions of all those given in the experiments where a yield is satisfactory are those under which 8, 9, and 10 were made.

Hence, it is clear that in presence of zinc chloride diethyl succinic ester is easily obtained in large amount closely approximating that theoretically possible from a known amount of succinic acid. This is most easily done by heating at a temperature about 100° succinic acid with alcohol containing a small amount of hydrochloric acid in presence of zinc chloride in small quantity, while gaseous alcohol is driven into the mixture.—*American Journal of Science*, xxiv., p. 194.

THE BEHAVIOUR OF MOLYBDIC ACID IN THE ZINC REDUCTOR.

By D. L. RANDALL.

There has been a difference of opinion in regard to the degree of reduction obtained when molybdic trioxide, in sulphuric acid solution, is passed through the column of amalgamated zinc as applied in the Jones reductor. Jones (*American Institute Mining Engineers*, xviii., 705), who first determined molybdenum by this method, considered that the reduction goes to the condition represented by the formula $Mo_{12}O_{19}$, the same degree of reduction that Wernke (*Zeit. Anal. Chem.*, xiv., 1) obtained with zinc and sulphuric acid in a closed flask. Doolittle (*Journ. Am. Chem. Soc.*, xvi., 234) and Eavenson found that, by varying the strength of the acid and the speed at which the molybdenum was passed through, different degrees of reduction might be obtained. They calculated no formula corresponding to the degree of reduction obtained by them which was lower than that represented by $Mo_{12}O_{19}$. W. A. Noyes and Frohman (*Journ. Am. Chem. Soc.*, xvi., 553), by taking pains to replace the air in the reductor flask by carbon dioxide, were able to obtain a reduction to the form of Mo_2O_3. Blair (*Journ. Am. Chem. Soc.*, xxvii., 747) and Whitfield, however, were unable to press the reduction below the condition represented by the symbol $Mo_{24}O_{37}$. Miller (*Journ. Am. Chem. Soc.*, xxv., 919) and Frank in repeating the experiments of Blair and Whitfield obtained in general the same results, though by taking extraordinary precautions they were able to get a reduction to a point a little below midway between the conditions represented by the symbols $Mo_{24}O_{37}$ and Mo_2O_3.

The ease with which the reduced molybdenum solution is oxidised by the air has been noted, and suggests the possibility of charging the reductor flask with some oxidiser unaffected by air, which shall anticipate the oxidising effects of the air as the reduced molybdenum compound comes through the reductor and register the oxidation.

In the first experiments an excess of a standard solution of potassium permanganate was used in the receiver. But it was found, by running blanks, that somewhat more than the theoretical amount of permanganate was used up. Table I. shows the results of experiments made by charging the reductor flask with 20 cc. of approximately tenth-normal standard potassium permanganate, passing 300 cc. of warm dilute (2·5 per cent) sulphuric acid through the reductor, adding 20 cc. of standard ferrous sulphate solution and titrating with permanganate to colour.

This excessive reducing action on the permanganate must be due either to impurities in the zinc, to small particles of zinc worked through the asbestos layer at the bottom of the reductor, or possibly to the hydrogen formed in the reductor. That the last mentioned possibility is a sufficient cause of the effects obtained was shown by passing hydrogen, formed by the action of hydrochloric acid on zinc in a Kipp generator and washed with water and caustic potash, through 23 cc. standard permanganate diluted with 300 cc. of hot dilute (2·5 per cent) sulphuric acid, adding 20 cc. of a solution of standard ferrous sulphate, and titrating back with permanganate. The results obtained by such action of hydrogen during fifteen minutes is shown in Table II.

Table I.

$FeSO_4$.	$KMnO_4$ used.	$KMnO_4$, theory.	Difference.
Cc.	Cc.	Cc.	Cc.
20	24·45	23·25	1·20
20	23·88	23·25	0·63
20	25·40	23·25	2·15
20	24·90	23·25	1·65

Table II.

$FeSO_4$.	$KMnO_4$ required.	$KMnO_4$ theory.	Reduced by hydrogen.
Cc.	Cc.	Cc.	Cc.
20	24·6	23·1	1·5
20	24·7	23·1	1·6
20	23·6	23·1	0·5

Having seen that potassium permanganate could not be used in the reductor flask, ferric alum was next tried as an oxidiser. The only objection to the use of this salt, that at the usual dilution of 500—600 cc. an excess of ferric alum colours the solution strongly and makes the end-point in the titration somewhat difficult to recognise, is overcome by the addition of a few centimetres of phosphoric acid which renders the solution colourless.

For the work with the ferric oxidiser the C. P. ammonium molybdate of commerce was re-crystallised and found to contain 81·55 per cent of molybdenum trioxide by treating weighed portions in a platinum crucible with nitric acid and evaporating to dryness on the steam-bath and igniting gently and weighing the molybdic anhydride formed. The ferric iron solution for use in the reductor flask was prepared by dissolving 100 grms. of the crystallised salt in one litre of water. The column of zinc in the reductor was 36 cm. in length. The procedure was to charge the reductor flask with 20 or 30 cc. of the iron solution and 4 cc. of phosphoric acid, and to pass through the reductor in succession 100 cc. of hot dilute sulphuric acid (2·5 per cent.), the ammonium molybdate dissolved in 10 cc. of water and acidified with 100 cc. of the hot dilute acid (2·5 per cent), 200 cc. of the hot dilute acid, and finally 100 cc. of hot water. The solution was titrated while still hot with approximately tenth normal permanganate standardised against ammonium oxalate.

The molybdenum as it passed through the lower part of the reductor was green, but on coming in contact with the ferric salt was changed to a bright red colour. The results in the following table are calculated on the assumption that the molybdenum was reduced to the form of Mo_2O_3. The close agreement with theory indicates that the reductor is able to reduce molybdenum to that form and that the reduction does not stop at a point represented by the formula $Mo_{24}O_{37}$ or $Mo_{12}O_{19}$.

Table III.

Ammonium molybdate taken.	Iron sol.	H_3PO_4.	$KMnO_4$ used.	MoO_3.		Error.
				Found.	Theory.	
Grm.	Cc.	Cc.	Cc.	Grm.	Grm.	Grm.
0·2000	20	4	30·38	0·1628	0·1631	−0·0003
0·2000	20	4	30·45	0·1632	0·1631	+0·0001
0·2000	20	4	30·33	0·1626	0·1631	−0·0005
0·3000	30	4	45·65	0·2447	0·2447	—
0·3000	30	4	45·80	0·2455	0·2447	+0·0008
0·3000	30	4	45·73	0·2451	0·2447	+0·0004
0·3000	30	4	45·76	0·2453	0·2447	+0·0006
0·3000	30	4	45·68	0·2448	0·2447	+0·0001
0·3000	30	4	45·64	0·2446	0·2447	−0·0001
0·3000	30	4	45·71	0·2449	0·2447	+0·0002

It having been shown that molybdenum may be successfully and uniformly reduced to the condition of Mo_2O_3 by anticipating any previous action of air and registering the oxidation by the action of a ferric salt, the method was then applied to the determination of phosphorus in ammonium phospho-molybdate precipitated in the usual manner.

For this work a solution of microcosmic salt was made up 1·2 grms. to the litre and the phosphorus content determined by evaporating 50 cc. in a platinum crucible and igniting to form the sodium metaphosphate.

With the exception of using an equivalent amount of ammonium molybdate instead of molybdic anhydride, the method given by Blair was used for making up the molybdate reagent ("Chem. Analysis of Iron, Sixth Ed., p. 97). According to this method, 100 grms. of pure molybdic anhydride and 400 cc. cold distilled water are thoroughly mixed and the mixture is treated with 80 cc. of strong ammonia (0·90 sp. gr.). When the solution is complete, the liquid is filtered slowly and with constant stirring into a mixture of 400 cc. of strong nitric acid (1·42 sp. gr.) and 600 cc. distilled water. Then 50 mgrms. of microcosmic salt dissolved in a little water are added, the mixture is agitated thoroughly, the precipitate is allowed to settle for twenty-four hours, and the solution is filtered before using.

In order to have iron present during the precipitation of the phospho-molybdate, a solution of ferric nitrate was prepared and used in each experiment. A solution of the C. P. ferric nitrate of commerce, $Fe(NO_3)_3,9H_2O$, was made up to contain 150 grms. to the litre, with enough nitric acid added to give the solution an amber colour. To free the iron solution from traces of phosphorus, 400 cc. of the molybdenum solution were added to the ferric nitrate and the whole well shaken and allowed to stand for twenty-four hours.

To measured portions of the phosphorus solution, in a 300 cc. Erlenmeyer flask, were added 150 cc. of the iron solution filtered and warmed to 35° C. The flask was stoppered with a rubber stopper and shaken for five minutes. The precipitated phospho-molybdate was allowed to settle, and was then filtered on asbestos in a perforated crucible and washed with a solution of ammonium acid sulphate (15 cc. ammonia, 25 cc. sulphuric acid, 1 litre water). The Erlenmeyer was washed out with a solution of 20 cc. of water and 5 cc. of ammonia, and this was poured on the asbestos in the crucible. The molybdenum solution was acidified with 10 cc. of strong sulphuric acid and was passed through the reductor into the ferric alum solution. The molybdenum solution was preceded by 100 cc. of hot water and followed by 200 cc. of the hot dilute acid and 100 cc. of water. The reduced solution was titrated immediately with approximately tenth normal permanganate. In the following table are shown results thus obtained in precipitating phosphorus as the phospho-molybdate, passing the acidic solution through the reductor into a solution of ferric alum, and titrating the ferrous salt which is formed.

TABLE IV.

P taken. Grm.	P found. Grm.	Error. Grm.
0·003645	0·003673	+0·000028
0·003645	0·003697	+0·000052
0·003645	0·003638	−0·000007
0·003645	0·003726	+0·000081
0·003645	0·003630	−0·000015
0·003645	0·003661	+0·000016

These results are calculated on the assumption that the ammonium phospho-molybdate contains phosphorus and molybdenum in the proportion given by the symbol $(NH_4)_3,12MoO_3PO_4$, and that the reduction proceeds to the condition represented by the symbol Mo_2O_3.—*American Journal of Science*, xxiv., p. 313.

THE DANGER OF OVER SPECIALISATION.*

By L. H. BAEKELAND.

(Concluded from p. 107).

AFTER the advent of Christianity, the despotic Church of Rome retarded the progress of all Christendom as soon as she tried to specialise all human knowledge, so as to make it agree with her own bible. The result was that long and sad period of the dark Middle Ages. In the meantime, Saracen and Jew, on the north coast of Africa, or on the Iberian Peninsula, were able to cultivate science less trammelled by a restrictive religion. To their broader activity do we owe it that scientific investigation was kept alive until the day when the dawn of Reformation enabled backward Christendom to resume again the search for truth.

But, even now, our educational system is still much under the chilling effect of that cloud during which the Middle Ages hid the light of true knowledge. Respectable pedagogues have taken care to hand us down from generation to generation a curriculum which includes most of what formerly was erroneously called *a complete education*. In the latter, ancient literature, holy or profane, has always played a paramount importance. In its programme scant consideration is given to more real modern knowledge which refers broadly to the world we live in, or to the burning questions of the day. I know of many instances where, under the name of liberal education, such an antiquated tuition is still dealt out to the younger generation of both sexes. In fact, many well-meaning persons think that this is the kind of respectable training most desirable for a rich young man of good family and good manners. In reality, such an education is merely an over specialisation of the kind of culture which was meted out to studious sons of patricians some two thousand years ago. For our modern requirements, it is an anachronism, if not a positive danger: a danger—because it is liable to select as standards the undeveloped or erroneous thoughts of antiquity. In many instances, the tendencies of the ancients clash with our more advanced ideas of truth and justice—even if the latter are not always consistently practised by modern society.

The French Revolution encouraged some reforms in this antiquated system of education. But even to-day modern science and modern thought are grudgingly allowed a very small place in the classic curriculum so faithfully defended by some pedagogues. Small wonder, then, if we hear so many respectable people use flowery rhetoric on such inconsistent themes as "science versus religion," or "science versus art"; as if there were any *versus* possible whenever we speak of science as true science, religion as true religion, and art as true art—as if truth were different, whether expressed scientifically, religiously, or artistically!

Luckily for the progress of humanity, now and then some young men, less blessed with worldly goods or wealthy parents, and more eager to make a living by their own work and education, have been compelled to give a vigorous kick to the classic curriculum fetish. Some of them decided to take their education "à la carte"—as President Eliot expressed it so picturesquely. They were compelled to select substantial and up-to-date meals, more suitable to their eager modern appetites; they had to shun the stale and indigestible dishes of education made up in antiquity, to please the palates of bygone times.

Unfortunately, the very cause of this new tendency has carried us so far as to seriously threaten us with the pitfalls of the other extreme.

Furthermore, the fact that scientific learning has found unceasing applications in the production of wealth has fostered the constantly increasing tendency for finding in scientific education or scientific pursuits a mere means of earning a living or making money. This has led into

* Read before the New York Section of the American Chemical Society. From *Science*, 1907, xxv., No. 648.

scientific vocations a large number of persons who in their profession expected to find a quick and easier means for making a living, but outside of this stimulant possessed few, if any, of the qualifications of the true scientist. Impractical in their selection, they deceived themselves by choosing an occupation which less than any other leads to wealth or power. But once having decided to enter a scientific profession, they soon became aware that the call is for specialists, and they were forced to specialise one thing or another by their employers, whether the latter were manufacturers, merchants, or even some educational institutions whom they served as teachers.

In accordance with this same tendency we find manufacturers who, themselves without other training excepting what long experience has taught them, blame our colleges, universities, or technical schools because they do not turn out graduate chemists who can jump right away into their manufacturing works fully acquainted with all the intricacies of the processes; of course, all this with the prospect of a small salary so as to act in competition with a few able and better paid men who had to sacrifice a lifetime in order to acquire experience.

That greed or ignorance should make such claims is quite natural; but that we should find teachers or students who are willing to admit such abnormal educational methods, and change them into a kind of apprenticeship, is a matter of regret for anybody who believes in education as a means for the healthy mental development of his country.

What is worse, our own way of living shows beyond doubt that we all have undergone, more or less, the effects of over specialisation against which I have come to protest. Too much have we learned to look upon our usefulness in life as depending almost exclusively on the concentration of most of our energies, most of our thoughts, upon a narrow line of specialised action. Without knowing it we drift into a mere routine occupation that makes automatic machines out of us. For all generalities of life which do not fall immediately into our own specialities, we are willing to assume respectable conventionality: We are willing to join the herd of docile and unthinking sheep who are following a leader. In science as well as in politics, we are ready to follow this leader, for better or for worse, as long as we can shift upon him our own responsibilities of thought or action.

Busily burrowing along like moles, in the pursuit of our own little specialities, we are dizzily preoccupied with our specialised routine work. We lose the desire of coming once in a while upon the surface of the earth to take a stimulating look at the grand view of nature and its inspiring entity. Once upon a while, we are rather disturbed in our narrow scientific beliefs when some Curie announces radium or radio-activity, or when some Ramsay upsets our orthodoxy by pronouncing the words: evolution of elements. We get fairly shocked when a Crookes speaks of death of matter.

Just in the same way, after admitting as holy faith that weight and matter are constant or indestructible, some day, somebody may have to rouse the most timid of us and force us into the belief that gravitation, like all other energies, can be modified into any of them, or better perhaps, that gravitation, being the more stable of all energies, is the final energy toward which light, heat, and electricity tend to change. Who knows but that ultimately a less neglected study of gravitation may allow us a glimpse into the secret of the destiny of our universe?

I admit many of you will smile at these unorthodox hypotheses or conjectures. Yet, let me ask you: With what methods have we thus far measured any possible changes in weight? We have pinned all our faith, all our beliefs, on a mechanical instrument called a balance. A very delicate method indeed, if judged from our conceited one-sided standpoint of specialists. We are proud if we possess a balance which can weigh 1/100 of a mgrm.; we work ourselves into awe and admiration before an instrument such as the one I saw two years ago which can detect a difference of one-thousandth of a mgrm. A one-thousandth of a mgrm.! How infinitesimally small such a weight appears to our limited conceptions; and yet, what a ponderous quantity this same weight becomes if we try to compare it with the mass of an electron. Our whole science of chemistry is based on the fundamental law of the conservation of matter as formulated by Lavoisier and accepted by us as an axiom. However, by what means has this law been verified, if not by balances more crude, more imperfect, than that clumsy instrument which cannot weigh anything beyond 1/1000 of a mgrm.? It is high time that science should discover a more delicate means for determining small weights than a mere mechanical balance; then, but only then, may we be able to demonstrate beyond doubt whether all the assumptions on which we base our chemistry are correct, or whether we simply have been building a whole science on false premises.

While we are at this subject let us continue this act of self-examination. When we speak of the descriptive part of the science of chemistry, when we describe any reactions, any compounds, any laws, we all refer these to phenomena which take place within an abnormally small range of temperature. Lately, Dewar opened our eyes to some unexpected phenomena which occur at very low temperatures; on the other hand, the electric furnace so ably manipulated by our regretted Moissan enabled him to establish many unsuspected facts at temperatures which our imperfect thermometric methods do not allow us to measure accurately. Yet, if we will drop for a moment our one-sided considerations and look upon everything in true proportions, we must admit that the range of temperatures within which we have studied natural phenomena is disappointingly small, as compared with the possible range of temperature of the universe.

Not so long ago, chemists had no better definition for organic compounds than to designate them as those that were produced under the intervention of vital forces; inorganic bodies, on the contrary, were supposed to be made under the influence of ordinary physical forces. We all know since how Liebig and Wöhler disposed of this mistake by the memorable discovery of the synthesis of urea from inorganic bodies. Nevertheless, many of us to-day are prone to think that the more delicate organic bodies, as, for instance, the constituents of the protoplasm, will never be obtained synthetically. These doubters point to the fact that as soon as we try to imitate these subtle, synthetic reactions which take place in the living cell we remain powerless to accomplish anything beyond splitting or simplifying the molecule. And yet, let me ask you, what are the laboratory methods with which we try to imitate the subtle biological processes? Heating, boiling, distilling, desiccation, precipitation, electric currents, every one of them barbarously destructive methods, with which we blast away at exceedingly delicate compounds. We might just as well try to imitate the melodious music of a Gounod by firing some dynamite cartridges between the delicate strings of a piano?

One-sided as we are, we witness every day of our lives the fact that all vegetation accomplishes its processes of synthesis or assimilation under the indispensable action of light; nevertheless, thus far we have tried very little to avail ourselves of this powerful yet delicate source of synthetic energy. Up till now photochemistry has scarcely been used for any other purposes but the art of photography.

What have we done to utilise the effect of pressure in the study of natural phenomena? Very little, even if we take in consideration some half-hearted attempts in this direction. What are the pressures we dispose of as compared with those which exist in the centre of the earth? We hear of mines about one mile deep of which the tunnels are submitted already to such a tremendous natural pressure that their walls snap together shortly after an excavation is made, leaving the miner barely time to get out, so as to save his life. If we calculate the pressures existing at these depths we come to very awe-inspiring figures. But

if again, we invoke the sense of proportions, we must recognise that a mine one mile deep is a mere insignificant and imperceptible pin prick as compared to the size of the earth. After such considerations, can we expect to duplicate certain chemical or physical processes which have been going on under tremendous pressures in the bosom of the earth? Or shall we try to find means to enormously increase the pressures of which we have thus far disposed in our laboratories, and have considered sufficient, although they are absurdly small.

And how about the element of time in chemical reactions? We all now are aware of the fact that even an explosion of dynamite takes an appreciable and measurable time. On the other hand, Berthelot, in his memorable studies on esterification, has demonstrated that in some cases it requires sixteen years of continuous action before the limit of esterification is reached and a final equilibrium is maintained. We are not inclined to patiently study reactions which take months or years, and yet, in the great laboratory of nature, phenomena are accomplished just the same whether their fulfilment requires seconds or æons. But in our lives, which are of such an infinitesimal shortness if compared with eternity, we look at everything according to the very short lapse of time which is allotted to our little individual existence. We refer and compare everything to it, in about the same way as I suppose the may-fly does to her own little life, after she has become accustomed to the fact that her existence is counted only by a few hours.

I am perfectly aware that these and many other philosophical conceptions are receiving consideration from such broad-minded scientists as have not grown up to consider science as divided in water-tight compartments. For them the borderland between the different fields of specialised science becomes the favourite hunting-ground for the philosopher. To the latter, scientific pursuits mean something broader, something higher than a mere concentration on a special field, to the exclusion of all others.

On the other hand, over-specialised science is apt to degenerate into a mere hobby, where all conceptions of true proportions and harmony are lost. The corner grocer who knows all about the prices and qualities of sugar, coffee, and tea, and little else, is nothing less than an exaggerated example of over-specialised knowledge. In the same way, I am sorry to say it, I have met many an example of so-called scientists whose science does not rank higher than what is involved in the pursuits of my boy when he is eagerly engaged in the collection of cancelled postage stamps. Knowledge does not contribute necessarily to the wisdom of the individual, unless that knowledge be sufficiently diversified to stimulate his thinking powers. The scientist who spends all his time in purely theoretical work and looks down upon the man who tries to find industrial applications for our knowledge, shows just as much unwarranted one-sidedness as the so called "practical" man or empiricist who expresses contempt for purely scientific pursuits.

For fear that I may be misinterpreted, let me repeat that I shall be the last to deny that every one of us is compelled to specialise more or less, in order that we may become thorough in some one branch of human activity and in order to develop our individual usefulness. I am aware that even the dullest specialist, who does conscientious work, will be of some use to the community: If he be engaged in scientific research work, and carefully records well-observed facts, he renders a service to mankind; he presents us with his own home-made little bricks, which in time will be used by the architects of science to build up the ever-increasing edifice of knowledge.

I hope, I need scarcely add, that I further believe that well-recorded scientific facts of small immediate importance may in time become immensely valuable as compared with elegant but wrongly conceived theories based on hasty generalisations.

I believe, also, that in these times of unbalanced industrialism and greed, the law of self-preservation commands us to select a speciality as a bread-winning pursuit. I am fully aware that insufficient pecuniary resources compel many of us to curtail our preliminary studies to the very minimum consistent with what we absolutely need so as to enter into a remunerative trade or profession.

But however light-weighted our educational baggage may be, when we enter practical life, nothing but our own indifference, our bad judgment, our lack of aspiration towards nobler aims, prevents us from remedying this. Every day of our life, as long as we live, is given to us for increasing by self-culture the slender outfit with which we left school. And self-culture, in order to be effective, ought to be directed so as to counteract any one-sided tendencies resulting from our specialistic daily occupations.

The majority of individuals give by far the largest amount of their work, their endeavours, their thoughts, to the production of wealth, or to put it simpler: the art of making money. Yet, engrossed as we are in this one-sided occupation, very few of us think it worth while to undertake the study of that science which investigates the laws of production and distribution of wealth. Ignoring the true, if elementary, principles of political economy or believing in a perverted political economy which has been invented to serve the ends of a few as against the rights and interests of the many, we help to perpetuate the main cause of numerous social ailments. The scant attempt of serious attention which is given to this branch of knowledge by any but a few specialists, has rendered possible the exaggerations and irregularities of our system of industrialism. It has helped to keep in bondage many deserving men of exalted character, but unable to develop their possibilities, as they might do, under a wiser system. Who does not know of some otherwise highly developed individual who now is treated with contempt because he committed the crime unpardoned by our modern society, of failing to master that greedy art of accumulating money for himself, or for others.

Over-specialists as we are in our daily pursuits, we are ever prone to scorn the politicians; we think we have done all our duties as citizens if on election day we take time to cast our vote instead of standing all day on the golf links, but only to find out afterwards that we have supported men who, through ignorance and selfishness, hoodwink us and prevent us making our country the true democratic republic so simply and forcibly defined by Lincoln as: a government of the people, by the people, and for the people.

If we have any fault to find with our politicians and lawmakers we should blame none but ourselves and that tendency of over-specialisation which keeps us in our own narrow routine and lets the politician-specialist rule us and the country as well.

If political economics is a science of momentous interest to everybody alive, it is specially of interest to the chemist, who, thorough believer in the laws of nature, can not fail to admit the same universal yet simple laws in sociology; and who, therefore, is less apt to be misled by those juggleries of reasoning which are so cleverly used to favour private interests against the weal of the community at large. Political economy, different from most sciences, can be mastered without any preparation whatsoever, excepting the relinquishment of all bias and all petty ideas of greed, conceit, or inequity.

But what shall I say about our criminal neglect of eugenics, a science which goes to the very roots of our lives; a knowledge which deals with the future of our children, the happiness and betterment of our race, and yet so neglected that its very name is scarcely known in our usual vocabulary. In the meantime, we go on in our happy-go-lucky-slipshod way; we assume the tremendous responsibility of parentage, and we jeopardise the health and happiness of our children and grandchildren by our carelessness. Instead of trying to bring together in marriage, by orderly, careful, and methodic selection, such persons as are physically and mentally best fit for ennobling our race, we leave this important matter entirely to the whim of chance, blinded

by emotion or prejudice. Our actions in this as in many other instances, are but the logical outcome of a thoughtless one-sided education which does not deal with these subjects, while under the name of *belles-lettres* our thoughts are still further perverted in prose and in rhyme by romantic novelists, who in their own way write on the subject of love and marriage. Neither should we be astonished, if frequently those who feel proudest or brag loudest about their ancestry make very light work of their own lives, as far as their actions involve any responsibility towards their offspring.

Our one-sidedness of conceptions has fraught our whole social system with inconsistencies: we grant the unwarranted privilege to vote to illiterate blacks and whites, tramps, or idlers; but from the intelligent, virtuous, and active woman who is the mother of our children we absolutely withdraw the *right* to participate in the affairs of the nation.

Our lack of broad-mindedness is shown in many other ways. We admit the principle of evolution, but when it comes to concede rights and friendliness towards animals —fellow-beings—we fall short of our theories: we eagerly forget that other living creatures enjoy life and suffer, feel, and think as we ourselves, if not exactly in the same way. Some of us claim to be civilised, and yet find high pleasure and recreation in hunting, killing, maiming, and torturing defenceless animals, although we go on criticising the Spaniards who enjoy the gore of a bull-fight. And even those of us who admit the savage cruelty of hunting and kindred sports do not hesitate to elevate, propagate, and degenerate certain species of domestic animals with the express purpose of killing them for food. We do not see anything inconsistent in the fact that, scientific though we are, and while we talk snobbishly of our refined taste, we are much less particular than plant-eating animals, and we keep feeding on corpses of fellow creatures.

We call ourselves scientists because we believe in the laws of nature. In our studies and our research work we have never-ending opportunities for admiring the marvellous harmony of nature, the invariable laws of God. Yet when we hold our annual banquet of scientists we fail to see that we blaspheme the God of law and order and deny the immutability of his laws by asking him in prayer (and in this similar to savages) to disturb these eternal laws of nature so as to grant us some petty favours, forgetting that we are merely insignificant little dots in the immensity of the universe.

Let me conclude this essay by repeating the main points mentioned therein:

If specialisation may be advantageous for increasing our productiveness in a given field of activity, over-specialisation, on the other hand, may develop one-sidedness; it may stunt our growth as men and citizens; even for persons engaged in scientific pursuits it may render impossible the attainment of true and general philosophic conceptions.

If I have succeeded in convincing some of us that over-specialisation does not bring forth the very best there is in us, if I have contributed ever so little to keep us aloof from the life of dizzy automatic machines, if I have succeeded even in the smallest degree in stimulating you to nobler endeavours, then I shall indeed feel very amply rewarded by your kind attention.

Synthesis of Racemic Dihydrocamphoric Acid.—L. Bouveault and R. Locquin.—Alkyl cyclopentanone carbonic ester can be transformed by the action of alcoholic potash in excess into the potassium salt of adipic α-alkyl-substituted acid. With absolute alcohol the ethyl ester of the same acid is obtained. Disubstituted cyclic ethers behave similarly, giving α and α' substituted adipic ethers. The authors have used this method to synthesise α-methyl α'-isopropyladipic acid. The active form of this acid (dihydrocamphoric) has already been obtained by fusing camphoric acid with caustic potash.—*Comptes Rendus*, cxlvi., No. 2.

PROCEEDINGS OF SOCIETIES.

THE INSTITUTE OF CHEMISTRY.

Annual General Meeting, March 2nd, 1908.

Prof. Percy F. Frankland, LL.D., F.R.S., President, in the Chair.

The Thirtieth Annual Meeting of the Institute of Chemistry was held at 30, Bloomsbury Square, on Monday, March 2, 1908.

The Annual Accounts were received on the motion of Mr. A. Gordon Salamon, the Hon. Treasurer, who said that, owing to the increase in the number of candidates for the Examinations and the exercise of proper economy in expenditure, the year 1907 was financially one of the most satisfactory for the Institute within recent years. He remarked, however, that the work of the Institute was growing, and that therefore greater funds would be required, especially in view of the approaching expiry of the lease of the Institute's house. The Annual Subscription, a guinea, was lower than that of almost every other professional body, and he thought that the time had come for considering the desirability of raising the subscription so as to enable the Institute to extend its work on behalf of the profession.

Mr. E. W. Voelcker, in seconding the reception of the accounts, agreed with the Treasurer's suggestions as to raising the subscription, which was also supported by Mr. C. Sordes Ellis.

In moving the adoption of the Report of Council, Mr. David Howard remarked that only those who could remember the time when there was no organisation of professional chemists knew what it was to be without the Institute. The public now realised that there were other chemists than the pharmaceutical chemists, and, whether consulting practitioners, works chemists, or teachers, they could but admit that very important work had been done during the past year both by way of holding examinations for the hall-marking of young members of the profession, and of action taken to safeguard their interests. He alluded briefly to the recently published Report of the Committee appointed by the Treasury to enquire into the working of the National Physical Laboratory. It had not perhaps conceded all that the Institute asked, but it had met them to a considerable extent, and the profession was indebted to the Council for what they had done in that matter. The Examinations of the Institute were real, practical, and useful, and had exerted an enormous influence on chemical training in British universities and colleges.

The motion was seconded by Mr. G. T. Holloway, who said he knew that the Fellows and Associates warmly appreciated the work of the Institute in maintaining the status of the profession.

Scrutineers having been appointed to examine the votes for the election of the Officers, the Council, and Censors, the President delivered his Address.

He said that the Annual Report showed that the past year was one to which the Fellows and Associates could look back with satisfaction, as it bore evidence of distinct progress and healthy development. The membership had increased, there was a marked advance in the number of entries to the examinations, the Library had been extended, and the finances were in a more satisfactory state. On the occasion of every annual retrospect, however, they were reminded of the mortality of man. The year 1907 proved very fatal to chemists of the highest distinction throughout the world, terminating as it did the labours of Berthelot, of Mendeleeff, of Moissan, and of Perkin, all of whom would be remembered as amongst the greatest masters of chemical science. He referred to the rare intuitive genius of Perkin, and the extraordinary influence which his discoveries had exerted on both science and

industry, and said it was remarkable that he had transmitted so large a measure of his inspiration to the gifted family of chemists he had left behind. Of the other Fellows whom the Institute had lost by death, he made special mention of Dr. Dupré, for many years regarded as a distinguished leader of professional chemists; Dr. Macfadyen, the first Director of the Lister Institute; Dr. John Clark, President of the Society of Public Analysts; Mr. Samuel Hall, Treasurer of the Society of Chemical Industry; Mr. Montague Page; Mr. Richard John Friswell, a Past Vice-President and one of the most active workers for the Institute; and Mr. William Ashwell Shenstone, F.R.S., who had only recently served on the Council.

After referring to the splendid services of the retiring Officers and Members of Council, particularly mentioning Dr. Ed. Divers, F.R.S., and Mr. Edward Bevan, the retiring Vice-Presidents, and Prof. G. G. Henderson, the retiring Examiner, the President commented on the recent addition to the Board of Examiners of Prof. Herbert Jackson (to examine with Mr. Bertram Blount in the Intermediate Examination) and Prof. W. H. Perkin, F.R.S. (to examine in Organic Chemistry).

Continuing, the President dealt with the difficulties of students in deciding the most advisable method of preparing for admission to the profession of chemistry. He advised all serious students to aim at the Associateship of the Institute, and to shape their courses of studying according to its Regulations. Without the qualification of the Institute they would greatly restrict the field in which they could seek employment. The requirements of the Institute tended to broaden the base of chemical training, and could only usefully benefit the student in whatever branch of chemistry he might subsequently engage. He advised them to work for Degrees with high honours in chemistry concurrently with their preparation for the professional examinations of the Institute, so that they might be entitled to claim exemption from the Intermediate Examination. The Institute, by making a regulation to this effect, had put a high premium upon University study, and prevented unnecessary multiplication of examinations. He was sure that the leniency of the Examiners in the Universities did not extend so far as to place any but really satisfactory candidates in the first or Second Class Honours Divisions, and statistics had shown that they had been as successful in the Final Examinations of the Institute as candidates who had passed its Intermediate Examination. It was usually necessary for the candidate, after taking the Honours Degree or passing the Institute's Intermediate Examination, to obtain special training extending over at least a year before proceeding to the Final Associateship Examination. He was convinced that the usual three years' curriculum was wholly inadequate, for whilst the ground to be covered in the study of chemistry had attained colassal dimensions compared with what it was twenty-five years ago and was continually being extended, the students' time was no more protracted than before. The limited time at the disposal of the student gave him little opportunity to take proper advantage of the excellent equipment now to be found in the universities and colleges, and teachers were aware of the urgent necessity of increasing the minimum length of the curriculum prior to graduation, but no University appeared to have the courage to initiate this reform. In the matter of students, it was quality not quantity that universities required, for every science student was a net loss financially, and the work of the classes was too often hampered by a large proportion of undesirables.

On the motion of Prof. J. Millar Thomson, seconded by Mr. Bertram Blount, a cordial vote of thanks was accorded to the President for his Address.

Mr. Blount, in the course of his remarks, alluded to the evidence given by Prof. Frankland before the National Physical Laboratory Committee, and said that so far as the result of the action of the Institute on this matter had been satisfactory, it was greatly due to the fair and convincing manner in which the President had represented the views of the chemical profession.

The President having replied, the Report of the Scrutinerers was received. The following were elected Censors:—Mr. Russell Forbes Carpenter, Mr. David Howard, Sir William Ramsay, and Prof. J. Millar Thomson.

Mr. Percy A. E. Richards, Mr. Walter F. Reid, and Mr. G. T. Holloway were elected Hon. Auditors, and the Officers and Council were declared elected as follows:—

President—Percy Faraday Frankland, LL.D., Ph.D., F.R.S.

Vice-Presidents—Martin Onslow Forster, D.Sc., F.R.S.; Oscar Guttmann, M.Inst.C.E.; Egbert Grant Hooper; David Howard; Herbert Jackson; Sir William Ramsay, K.C.B., LL.D., F.R.S.

Hon. Treasurer—Alfred Gordon Salamon, A.R.S.M.

Members of Council—Leonard Archbutt; Julian Levett Baker; Adrian John Brown, M.Sc.; Russell Forbes Carpenter; Frederick Daniel Chattaway, M.A., D.Sc., F.R.S.; Harold Govett Colman, M.Sc., Ph.D.; John Henry Coste; Bernard Dyer, D.Sc.; Henry John Horstman Fenton, M.A., Sc.D., F.R.S.; Walter William Fisher, M.A.; Henry George Greenish; Otto Hehner; George Gerald Henderson, M.A., D.Sc.; William Richard Eaton Hodgkinson, Ph.D.; Arthur Robert Ling; William Macnab; George McGowan, Ph.D.; Gerald Tattersall Moody, D.Sc.; Henry de Mosenthal; Henry Droop Richmond; Kennedy Joseph Previté Orton, M.A., Ph.D.; John Edward Stead, F.R.S.; Francis Napier Sutton; Robert Rattray Tatlock; Oliver Trigger; John Augustus Voelcker, M.A., B.Sc., Ph.D.; Alexander Forbes Watson, B.Sc.

With a vote of thanks to the retiring Officers and Members of Council, moved by Dr. J. A. Voelcker, seconded by Mr. Salamon, and to which Dr. E. Divers and Col. C. E. Cassal responded, the meeting terminated.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 2, January 12, 1908.

Density of Graphite.—H. Le Chatelier and S. Wologdine.—Already noticed.

Transformation of Solutions of Yellow Phosphorus into Red Phosphorus.—Albert Colson.—The author has established the parallelism between the transformation of yellow into red phosphorus in the free state and when the substance is dissolved. The transformation occurs more quickly the higher the temperature. The time necessary to bring about the commencement of the transformation is approximately inversely proportional to the concentration of the solution when a given temperature is maintained. If "vapour tension" is substituted for "concentration" it is clear that the transformations in solution and in the free state are strictly comparable. The two processes are, however, not identical, and the presence of a solvent retards the transformation.

Constitution of Manganese Cast-Irons.—L. Guillet. Cast-irons containing small amounts of manganese when examined micrographically reveal the process of sorbite and carbide, while those containing more manganese consist of much carbide surrounded by a eutectic which the author has now found to be the eutectic mixed crystals—cementite. Manganese cast-irons, like nickel cast-irons, contain γ ferrite when the amount of manganese or nickel is large enough, but in manganese cast-irons a good deal

of carbide is present, increasing in amount as the percentage of manganese increases. A specimen containing 3·6 per cent carbon and 15 per cent manganese is made of practically pure eutectic. The addition of manganese to grey cast-iron produces γ-ferrite before causing the disappearance of graphite.

Ammoniacal Cuprous Sulphate.—M. Bouzat.—By adding cuprous oxide, ammonium sulphate, and alcohol to aqueous ammonia a precipitate is obtained. After being dried at the ordinary temperature of the air it loses about 1 per cent of its weight when the temperature is raised to 60—80°. Its composition is then represented by $SO_4Cu_2{\cdot}4NH_3$. When it is quite dry it is stable in air, but if it contains small quantities of mother-liquor it instantly oxidises, turning green and generating heat. It is decomposed by water, giving a precipitate of cuprous oxide. It gives a precipitate of copper with dilute sulphuric acid, and a solution of cupric sulphate and ammonium sulphate.

Synthesis of β-Campholene Lactone.—G. Blanc.—αα-Dimethyladipic ether when treated with sodium in toluene, gives a sodium derivative which by the action of ethyl bromacetate is converted into 3-dimethyl 3-cyclopentanone-2-carbonic-1-acetic ether. This ether is saponified to 3-dimethyl 3-cyclo-pentanone-2 acetic acid by boiling with hydrochloric acid. The ethyl ether of this acid yields a bitertiary glycol and a lactone which is β-campholene lactone.

Constitution of Isosparteïne.—Charles Moureu and Amand Valeur.—Isosparteïne appears to be derived from sparteïne by the transformation of a piperidine chain into a pyrollidine chain. The formula proposed for isosparteïne, which agrees with the value found for its molecular refraction, represents it as a bitertiary base, saturated, and not methylated at the nitrogen. All these properties belong to it in common with sparteïne.

No. 3, January 20, 1908.

Radio-lead.—B. Szilard.—The author has studied the conditions in which it is possible to separate radium D, E, and F from radio-lead when the latter undergoes certain chemical reactions. The re-crystallisation of the nitrate in a neutral solution separates the polonium (radium F) which remains in the solution, but has no effect upon the radium D and E which remain in the crystals. In an acid solution radium E is left in the solution. With the chloride the same separation is effected rapidly and completely. When radio-active lead carbonate is dissolved in concentrated sulphuric acid, and the filtered liquid is evaporated to dryness, the quantity of radium D in the residue is greater than that corresponding to the radio-active equilibrium of the radium E and F present. Nevertheless, there is only a slight concentration of the radium D in the product. Commercial urea gives a precipitate which contains a large part of the radium E and F in the solution but very little radium D, and ammonium carbonate gives the same result. These and other results show that it is easy to concentrate radium F, but much more difficult to concentrate radium D.

Synthesis of Ammonia.—M. Woltereck.—When mixtures of air and hydrogen are passed over iron sesquioxide ammonia is obtained, the most favourable temperature for the reaction being 300—350°. Better results are obtained when water vapour and air are passed over heated turf, and sugar carbon can also be employed. Thus small quantities of ammonia are formed during oxidations in presence of water, provided that the temperature does not exceed 700°.

Catalytic Power of Silica and Alumina.—J. B. Senderens.—Experiments upon the catalytic power of silica and alumina have shown that when silica is precipitated from sodium silicate or aluminium silicate at a moderate temperature it acts as a dehydrating catalytic agent towards alcohols, and gives pure ethylene compounds. But if the silicates are strongly heated for a long time the catalytic power tends to change, and the silica becomes a dehydrogenating agent. Exactly the same holds good for alumina.

Heat of Solution of Alkali Metals and Heat of Formation of their Monoxides.—E. Rengade.—The author's determinations of the heats of solution of the alkali metals give the following results:—(Na,Aq) = 44·1, (K,Aq) = 46·4, (Rb,Aq) = 47·25, (Cs,Aq) = 48·45. The heats of solution of their monoxides are:—(Na_2O,Aq) = 56·5, (K_2O,Aq) = 75·0, (Rb_2O,Aq) = 80·0, (CS_2O,Aq) = 83·2. This gives the following values for the heat of formation of the monoxides:—(Na_2,O) = 100·7, (K_2,O) = 86·8, (Rb_2,O) = 83·5, (Cs_2,O) = 82·7. These figures show that the affinity for oxygen decreases as the atomic weight increases.

Determination of Carbon Disulphide in Benzene.—Isidore Bay.—Phenylhydrazine gives with carbon disulphide a white crystalline precipitate of formula $CS_2(C_6H_5{-}NH{-}NH_2)_2$. The precipitation is complete after two or three hours. The precipitate is then filtered off through double weighed filter-papers, carefully washed with benzene, and dried in a vacuum. By this method carbon disulphide can be very accurately determined in commercial benzenes.

Transformation of α-Oxyacids into Aldehydes by Boiling an Aqueous Solution of their Mercuric Salts. Application to Preparation of *l*-Arabinose.—Marcel Guerbet.—By boiling for some hours mercuric lactate is decomposed into mercurous lactate, lactic acid, aldehyde, and carbon dioxide almost quantitatively according to the equation $2(C_3H_5O_3)_2Hg = (C_3H_5O_3)_2Hg_2 + C_3H_6O_3 + C_2H_4O + CO_2$. This reaction is not peculiar to lactic acid, but is common to all acids having an OH in the α-position. Thus the mercuric salt of gluconic acid, $CH_2OH{-}(CHOH)_4{-}CO_2H$, gives *l*-arabinose, $CH_2OH{-}(CHOH)_3{-}CHO$. The mercurous gluconate is rapidly decomposed into mercury and mercuric gluconate, which again undergoes the same change.

Simultaneous Production of 1.6 and 2.7 Dimethylanthracene.—James Lavaux.—In the following reactions the author finds that the product is not a single anthracene but a mixture of the two dimethylanthracenes 1.6 and 2.7:—I. Action of CH_2Cl_2 on toluene in presence of $AlCl_3$ (Friedel and Crafts). II. Action of $CHCl_3$ on toluene in presence of $AlCl_3$ (Elbs and Wittich). III. Action of $C_2H_2Br_4$ on toluene in presence of $AlCl_3$ (Anschütz). IV. Action of $AlCl_3$ on toluene (Anschütz and Immendorff). V. Action of $C_6H_5{-}CH_2Cl$ on toluene in presence of $AlCl_3$ (Friedel and Crafts). VI. Action of $AlCl_3$ on xylyl chloride (Friedel and Crafts). VII. Dimethylanthracene from coal-tar (Zinck and Waschendorff). The first of these anthracenes fuses at 240° and the other at 244·5°, and they form a mixture which fuses exactly at 225°. This is the lowest melting-point which the author has found for different mixtures of the two substances, and must therefore be the melting-point of their eutectic. The two constituents can be separated by combining chemical and physical methods.

Syntheses by means of Methyl and Ethyl Adipates.—L. Bouveault and R. Locquin.—Already noticed.

Action of Nascent Hypoiodous Acid upon Acids of Formula $R{-}CH{=}CH{-}CH_2{-}CO_2H$.—J. Bougault.—Phenylisocrotonic acid, $C_6H_5{-}CH{=}CH{-}CH_2{-}CO_2H$, is transformed into benzoylacrylic acid,—

$$C_6H_5{-}CO{-}CH{=}CH{-}CO_2H,$$

by the action of iodine in presence of a very large excess of sodium carbonate. The oxidation of the acid by alkaline potassium permanganate gives benzoic acid and oxalic acid, and reduction by sodium amalgam gives phenyl-γ-oxybutyric acid, $C_6H_5{-}CHOH{-}CH_2{-}CH_2{-}CO_2H$. The reaction which gives rise to benzoylacrylic acid may be represented by the equation $C_{10}H_{10}O_2 + 2O = H_2O + C_{10}H_8O_3$. The intermediate product formed is possibly

C_6H_5—CHOH—CHI—CH_2—CO_2H. The same reaction applied to *p*-methoxyphenylisocrotonic acid, CH_3O—C_6H_4—CH=CH—CH_2—CO_2H, gives an anhydrous acid which the author has as yet prepared in small quantities only. By analogy it should be *p*-methoxybenzoylacrylic acid.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 2nd instant, Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Colonel David Bruce, Miss Deane Butcher, Miss Cleghorn, Mrs. Dugald Clerk, Mr. V. Gordon, Mr. J. Hunter Gray, Miss Hassard, Mr. W. L. Preece, Dr. C. W. Saleeby, Dr. Hans Sauer, Mrs. Schilizzi, Miss Schilizzi, Mr. C. F. Wurtzburg, and Prof. H. A. Wilson, F.R.S., were elected Members. The Special Thanks of the Members were returned to Sir Andrew Noble, Bart., K.C.B., for his donation of £100 to the Fund for the Promotion of Experimental Research at Low Temperatures; to Mr. Shelford Bidwell for his Donation of £5 5s. to the General Fund; to Mr. W. Hugh Spottiswoode for his present of a Manuscript Record containing the early Laboratory Experiments of the late John Peter Gassiot, F.R.S., who was formerly a Manager and Benefactor of the Institution; and to Mrs. Kemp for her gift of a portrait of the late Sir Benjamin Baker, K.C.B., F.R.S., a Vice-President of the Royal Institution.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Heat of Combustion.—1. Has the heat of combustion of aluminium as $2Al+3O=Al_2O_3$ been experimentally determined? 2. If so, what is its calorific value expressed in calories per kilogrm. of substance (*i.e.*, Al), or in any other convenient measurement?—G. M.

MEETINGS FOR THE WEEK.

Monday, 9th.—Royal Society of Arts, 8. (Cantor Lecture). "Fuel and its Future," by Prof V. B. Lewes.

Tuesday, 10th.—Royal Institution, 3. "Membranes—Their Structure, Uses, and Products," by Prof. William Stirling, M.A., LL.D., D.Sc., &c.

Wednesday, 11th.—Royal Society of Arts, 8. "The Use of Reinforced Concrete in Engineering and Architectural Construction in America," by Ernest R. Matthews, F.R.S.E.

Thursday, 12th.—Royal Institution, 3. "Early British History and Epigraphy," by Prof. Sir John Rhys, M.A., &c.

—— Royal Society of Arts, 4.30. (Indian Section). "Progress of Native States during the past Forty Years," by Sir David W. Keith Barr, K.C.S.I.

Friday, 13th.—Royal Institution, 9. "Transatlantic Wireless Telegraphy," by Chevalier G. Marconi, D.Sc., &c.

—— Physical, 8. "Certain Dynamical Analogues of Temperature Equilibrium," by G. H. Bryan. "Experiments on Artificial Fulgurites," by Miss D. D. Butcher. "Distribution in Electric Fields of the Active Deposits of Thorium and Actinium," by S. Russ.

Saturday, 14th.—Royal Institution, 3. "Electric Discharges through Gases," by Prof. J. J. Thomson, F.R.S.

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THE CHEMICAL NEWS.

Vol. XCVII., No. 2520.

SOLIDIFICATION OF HELIUM.

On the evening of the 5th inst. Sir James Dewar received the following telegram, announcing the solidification of the last of the so-called "permanent gases"—helium :—

"Professor Dewar, Royal Institution, London.

Converted helium into solid. Last evaporating parts show considerable vapour pressure, as if liquid state is jumped over.

Kamerlingh Ohnes.

Leiden, 5th, 9 p.m."

To this Sir James Dewar replied :—

"Professor Ohnes, Leiden University.

Congratulations. Glad my anticipation of the possibility of the achievement by known methods confirmed. My helium work arrested by ill-heath, but hope to continue later on.

Dewar.

Royal Institution, 5th, 11 p.m."

THE OXIDATION OF FERROUS HYDRATE BY CUPRIC HYDRATE IN THE PRESENCE OF AMMONIA.

By HENRY R. ELLIS, B.Sc., F.C.S.,
and
W. HENRY COLLIER, F.C.S.

The fact that ammonia does not produce a blue colour when added to copper sulphate solution if ferrous sulphate is present has been noted by Levol (*Ann. Chim. Phys.*, lxv., 320).

This reaction has also been studied by Felix Hermann recently (*Chem. Zentr.*, 1907, i., 1394), and also by the authors (*Proc. Chem. Soc.*, xxiii., 235).

In the paper then submitted to the Chemical Society it was shown that certain conclusions of Felix Hermann were incorrect ; as these appear in the yearly report issued by the Chemical Society, the authors of the present paper have repeated their observations.

Hermann regards the non-appearance of the distinct blue coloration when NH_4OH is added to a solution of ferrous sulphate and copper sulphate, as being due to the reduction of cuprous salt which oxidises the iron ; he also states that the ferric hydroxide produced is insoluble in dilute H_2SO_4, and since his precipitate dissolved in cold dilute H_2SO_4 he concluded that the original ferrous sulphate was regenerated.

This the authors have shown to be quite incorrect ; *i.e.*, that ferric hydrate is soluble in cold dilute H_2SO_4, and, secondly, that the ferric salt remains as such, and is not reduced.

To ascertain the solubility of ferric hydrate in dilute H_2SO_4 the following experiments were carried out :—

1. Ferric hydrate was prepared by the addition of ammonium hydrate to a solution of ferric chloride, the precipitation was washed, and then added to $4N.H_2SO_4$, when it was immediately dissolved.

2. Another sample of the ferric hydrate was boiled with water for two hours, and after cooling was added to cold $4N.H_2SO_4$ and completely dissolved, but more slowly than before.

3. A third sample of ferric hydrate was dried for some time at 120° C., and was now partly insoluble in $4NH_2SO_4$; even on boiling the whole was not completely dissolved.

From this it is evident that the ferric hydrate is only difficult to dissolve in dilute H_2SO_4 when it has become partially dehydrated, and in the reaction between NH_4OH, $CuSO_4$, $FeSO_4$ such a condition is very improbable.

The precipitate in this reaction consists of ferric hydrate, ferrous hydrate, a cuprous body, and probably basic sulphates of copper and iron.

That this precipitate dissolves in dilute H_2SO_4 to produce ferrous and ferric sulphate is extremely easy to show. By using sufficient ammonia the whole of the iron is oxidised by the copper salt and ammonia, and dissolves as ferric sulphate with no ferrous sulphate. From the H_2SO_4 solutions cuprous chloride has been obtained by adding HCl.

Mixed solutions of $FeSO_4$ and of $CuSO_4$ were allowed to stand in closed flasks for varying times, with and without NH_4OH, the amount of which was also varied in different experiments. After standing, the solution was treated with dilute H_2SO_4 (20 cc. 4N), and titrated against N/10 $KMnO_4$.

The end-point was very distinct in all experiments carried out in the cold, but when the solutions were boiled the end-point was untrustworthy, and such experiments were not continued.

The following table will illustrate the experimental results :—

I. *Interaction in the Cold of Equivalent Quantities of* $FeSO_4$ *and* $CuSO_4$.

Time.	N/10 $FeSO_4$.	N/10 $CaSO_4$.	N/10 $KMnO_4$.
2 mins.	20	20	20
5 ,,	20	20	20
10 ,,	20	20	20
60 ,,	20	20	20
12 ,,	20	20	20

Therefore no reaction takes place under these conditions.

II. *The two Solutions Heated together on Water-bath out of contact with Air.*

Time.	N/10 $FeSO_4$.	N/10 $CuSO_4$.	N/10 $KMnO_4$.	
1½ mins.	20	20	19·3	(*a*)
	20	20	19·5	
	20	40	19·5	
	20	40	19·2	
10 ,,	20	20	18·6	
	20	40	18·275	

(*a*) A brown precipitate was produced, due to hydrolysis of the iron salt.

Therefore the $FeSO_4$ is slowly being oxidised.

III. *Equivalent Quantities of* $CuSO_4$ *and* $FeSO_4$ *with varying quantities of* NH_4OH.

	Time.	N/10 NH_4OH.	N/10 $CuSO_4$.	N/10 $FeSO_4$.	N/10 $KMnO_4$.
		Cc.	Cc.	Cc.	Cc.
1.	15 mins.	20	20	20	18·8
		20	20	20	18·8
		20	20	20	18·9
2.	35 ,,	20	20	20	18·1
		20	20	20	18·2
		20	20	20	18·0
3.	115 ,,	20	20	20	16·0
		20	20	20	16·1
		20	20	20	16·0
4.	16 hrs. 45 mins.	20	20	20	15·9
		20	20	20	15·8
		20	20	20	15·9

Therefore iron is oxidised by the $CuSO_4$ and ammonia, but only about one-fifth of the total is so charged, and the oxidation does not continue after a certain time if air is excluded.

	Time.	N/10 NH_4OH.	N/10 $CuSO_4$.	N/10 $FeSO_4$.	N/10 $KMnO_4$.
		Cc.	Cc.	Cc.	Cc.
5.	15 mins.	10	10	10	9·175
		20	10	10	8·7
		30	10	10	8·075
		40	10	10	6·1
		50	10	10	4·075
	4 hrs.	50	10	10	0·575
	15 ,,	50	10	10	0·6

IV. *Excess of* NH_4OH *and of* $CuSO_4$

When the bodies were present in the following proportion, 10NH_4OH, $CuSO_4$, and $\frac{1}{2}FeSO_4$, the whole of the iron was oxidised in a few minutes, and on dissolving in dilute H_2SO_4 two drops of N/10 KMO_4 solution produced a permanent coloration.

Conclusions.

1. The failure of the ammonia test for copper in solution is brought about by the ferrous sulphate present, which reduces the copper to cuprous compounds

2. The whole of the iron can be oxidised by copper sulphate and ammonia in a short time.

3. The copper dissolves as cuprous compounds, and the ferrous and ferric hydrates dissolve without the ferric sulphate being reduced.

4. The reaction between iron and copper salts in presence of ammonia is different from the reaction in acid solution, when copper and cuprous salts will reduce ferric compounds on prolonged boiling.

The Chemical Laboratory,
The Polytechnic, Regent Street, W.

NOTE ON THE DETERMINATION OF FERROUS IRON.

By NICHOLAS KNIGHT.

Robert Manzelius, in the Geological Survey of Sweden (Sveriges Geol. Undersökning), calls attention to a universal defect in the estimation of ferrous iron in minerals and rocks. He finds that a considerable error arises from grinding the rock in the ordinary way to a fine powder owing to the oxidation of ferrous to ferric iron. If the specimen is reduced to a coarse powder instead of being *finely* pulverised, a more accurate result is attainable. This source of error has hitherto escaped the attention of analysts.

We have investigated specimens of siderite with a view to determine the oxidation effect when the mineral is finely pulverised. In each case only the ferric oxide was estimated, and the method of Berzelius as modified and improved by Bunsen was employed.

About a grm. of the specimen was weighed each time in a 200 cc. flask, which was fitted with a bulb tube and Bunsen valve. The substance was dissolved in a small quantity of hydrochloric acid, and a crystal of sodium carbonate was introduced to make an atmosphere of carbon dioxide. The flask was cooled as quickly as possible with water, and the ferric iron was precipitated with barium carbonate. The precipitated iron was at once filtered with suction, and washed twenty or thirty times with cold water. The ferric carbonate was dissolved in hydrochloric acid, the excess of barium removed with sulphuric acid, and the iron precipitated with ammonia. The ores contained only about 1½ per cent of residue insoluble in hydrochloric acid. Two different specimens of the mineral were studied.

I. The specimen was run through a Taylor hand ore-crusher, and came out as a coarse powder. The mean of several fairly concordant results was 2·68 per cent Fe_2O_3. The coarse powder was next so finely ground in an agate mortar as not to feel gritty when placed between the teeth. It gave 3·26 per cent Fe_2O_3.

II. This specimen was enveloped in heavy paper, and reduced to a coarse powder in an iron mortar; 2·67 per cent of Fe_2O_3 was obtained. This coarse powder was finely ground in an agate mortar, when 3·11 of Fe_2O_3 per cent was obtained.

The oxidation is due to the heat caused by friction, and possibly in a lesser degree to the greater surface exposed to the air when the mineral is in a very finely divided state. The coarse powder is easily acted upon by the hydrochloric acid, and there is no necessity for making the determination with a very fine powder.

Our thanks are due to Mr. Robert H. Lott for making the analyses herein described.

Cornell College, February 12, 1908.

THE CHEMICAL ELEMENTS.

Periodicity, Weight, and Valency.

By GEO. WOODIWISS.

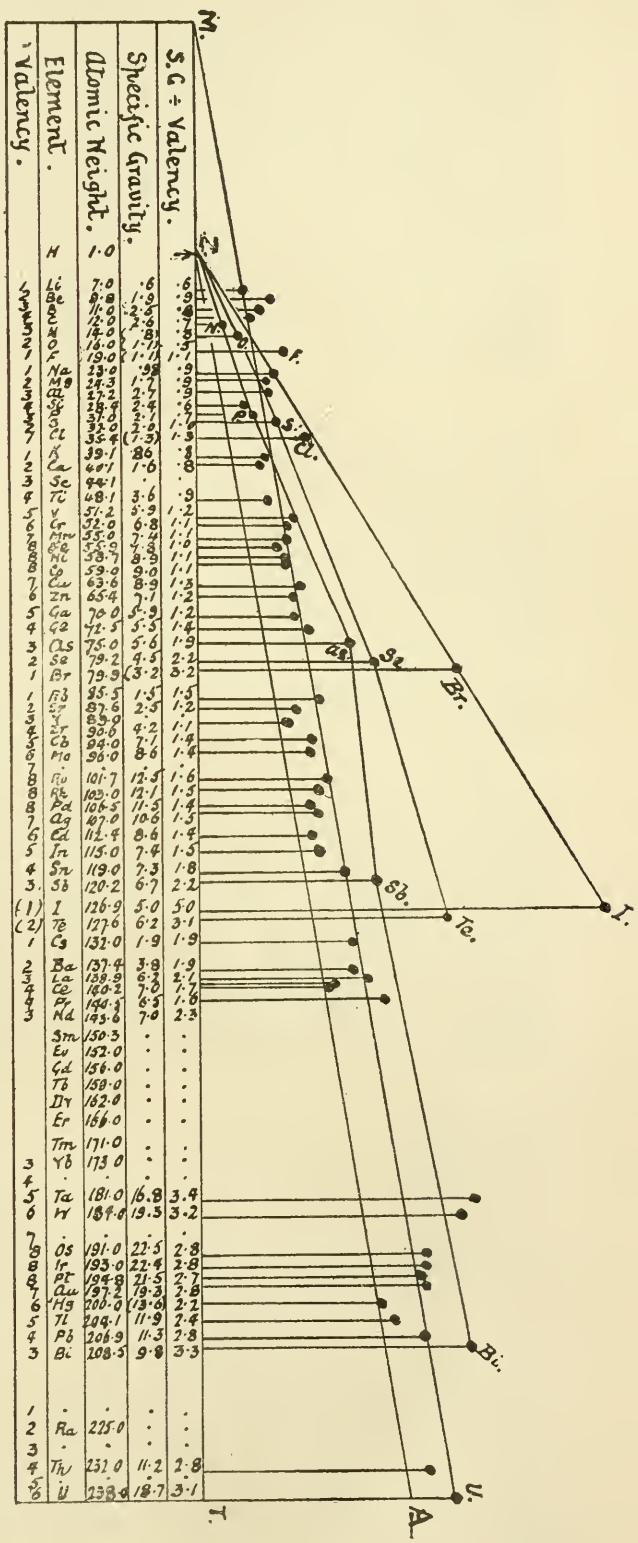
The atomic weight of copper is about three times that of sodium, the specific gravity is about nine times as great. Why should there be this great difference in relative weight in the two states? What is the order by which this difference takes place? At the first glance it would appear a very simple matter to obtain the relative weight of the elements in the solid state, but this is far from being the case; that is, under uniform conditions. In the first place, specific gravity is, and always must be, taken at a temperature wherein one element has an advantage over another in the amount of heat absorbed. Again, time, temperature, and pressure during solidification, and many other causes, tend to affect the ultimate result. Carbon, for instance, may crystallise from its solvent iron as graphite, or under increased pressure as the diamond. The diamond may be suitably heated, swell, and assume a coke-like mass. Each of these three states of the one element have a separate specific gravity. Phosphorus, platinum, sulphur, and others have allotropic forms. Silver in the molten state may absorb gases, large quantities of which are liberated on solidification, leaving cavities in the metal, and also probably affecting cohesion of the particles. Some elements at certain temperatures actually expand with reduction of heat. Traces of impurities and many others are the causes that may affect specific gravity. Given the elements in a perfectly pure state, solidified under exactly like conditions, and the ratio of weight at ordinary temperatures would at once be altered by alteration in temperature, for each element has a separate coefficient of expansion.

We must descend, therefore, to the lowest temperatures, to where the elements are totally devoid of heat, or rather, to where they are totally devoid of expansion, to obtain a truly comparative weight in the solid state. By Avogadro's theory we know that equal volumes of all gases under like conditions contain equal numbers of molecules. We therefore know that the molecular volume of all the various elements in the gaseous state is equal. On reviewing the ratio of weight in the solid state it is evident that this concordance has been upset; either there has been a change in the number of atoms to the molecule, or the molecular volume itself has changed for one element differently from that for another. When we consider the uniformity in volume of the molecules when charged with heat at the higher temperatures and the wonderful symmetry that nature delights in in all her laws, we must be prepared for regularity and symmetry in the atoms or molecules at the lower temperatures as well as at the higher. Allowing then a liberal margin for deviation, the accompanying diagram is constructed in an attempt to show that in all probability such is the case.

On the line M T are marked the elements at a distance from Z proportionate to their atomic weight. From M T perpendicular lines terminated by a dot are formed of a

length equal to the monovalent specific gravity; that is, $\frac{\text{specific gravity}}{\text{valency}}$. The valency employed is, perhaps, a new departure in periodicity, but is illustrated in a diagram (CHEMICAL NEWS, vol. xciii., p. 214). On the present diagram it is given by the bottom row of figures. It will be noticed these have a periodic rise and fall, commencing with an alkali and ending with a halogen thus, 1.2.3.4.3.2.1, 1·2·3·4·3·2·1, 1—8·8·8—1, 1—8·8·8—1. By this system of valency the copper group has a value of 7, and is therefore sharply separated from the sodium group, and the heavy metals generally are separated from the lighter ones. The most remarkable point, however, is—so far as the metallic elements are concerned—that the periodic rise and fall in specific gravity disappears, and an approximately regular increase is now in harmony with the regular increase in atomic weight. Atomic volume essentially depending upon specific gravity, it follows that the periodic rise and fall in atomic volume disappears, and that the periodic rise and fall in atomic volume is a function of valency. That is, so far as the metallic elements are concerned. With regard to the non-metallic and allied elements the case is different. To show this more clearly the line M U is drawn. In placing this line an endeavour is made to conform as nearly as possible to an average position indicated by the numerous dots. It will be noticed that most of the well known metals conform prettly closely to this line, the less well known metals and the non-metals generally being farthest away. We must not overlook the fact, however, that the specific gravity employed is taken at a temperature wherein absolute uniformity is not to be expected. It is evident that it is by no mere coincidence for the dots to fall on and about the line M U, and when we consider the uniformity in size of the molecule in the gaseous state, the enormous contraction that has taken place between that and the solid state, the great difference in boiling-points, melting-points, latent heats, &c., the close approximation to this line is remarkable. It is apparent that even at the intermediate temperature at which specific gravity is usually compared, there is an undoubted tendency for regularity in relative weight, and it is not at all improbable that were the elements totally devoid of expansion the weights would conform to some regular system of simple proportion.

In considering the alkali metals we find there is no indication of any system except a gradual increase in weight, as shown by the inclined straight line M U. Sodium has a deviation above and potassium below; but as there is a corresponding irregularity in vapour density, this may, perhaps, be attributable to some foreign cause. Taking, then, the ratio of weight of the alkali group as represented approximately by the straight line M U, then M U meeting M T at M we have at M a zero of weight for this group in the solid state. It is evident that the angle U M T may be made greater or less, but whatever alteration is shown thereby in the weight of one member of the group, a proportionate alteration is made for the rest of the group, and the ratio of weight is not altered; that is, providing always that the position of the zero M remains the same. If the ratio of weight of the group be altered then the zero must be altered to correspond. In a similar manner the zero of weight for the elements in the atomic state is at Z, and the angle, I Z T, may be varied to place the line I Z in various positions without any alteration to ratio of weight. But the line I Z cannot represent a ratio with the zero at M. If the angle I Z T is reduced until I Z is parallel with M U, then any weight represented by the line Z A is directly proportionate to the atomic weight. And as M U is parallel to Z A, it is evident that any weight represented by M U is equal to that of Z A plus a certain unknown quantity x, x being regulated by the distance of M U from Z A. Therefore the weight represented by M U is directly proportionate to atomic weight plus the unknown quantity x. We thus have specific gravity divided into two portions, one directly proportionate to atomic weight, the other a common quantity



x. The atomic volume may also be so divided and some remarkable calculations made, but it is not the purpose to enter into these here. Suffice that the zero of weight has moved from Z to M from the atomic to the solid state respectively, and that there must therefore be a corresponding change in ratio of weight.

It will be noticed the vertical lines are tangents of circles having a radius equal to the atomic weight of the elements. Thus, let hydrogen have a specific gravity of, say, 0·5, and the zero M be from the zero Z a distance of, say, 44 on the atomic weight scale, then a tangent at Z is 0·488, which is the distance apart of the lines M U and Z A. In the following table the Column A is atomic weight, B the tangent multiple, E the tangent at Z, F the calculated specific gravity, H the experimental specific gravity, K the difference between calculated and experimental specific gravity. The sodium gronp is taken with a valency or value of 1 and the copper group with a valency of 7.

		A.	B.	E.	F.	H.	K.
Li	1	(7·03	× 0·011	+ 0·488) =	0·57	0·59	− 0·02
Na	1	(23·05	× 0·011	+ 0·488) =	0·74	0·98	− 0·24
K	1	(39·11	× 0·011	+ 0·488) =	0·92	0·86	+ 0·06
Ru	1	(85·43	× 0·011	+ 0·488) =	1·43	1·5	− 0·07
Cs	1	(132·89	× 0·011	+ 0·488) =	1·96	1·88	+ 0·08
Cu	7	(63·60	× 0·011	+ 0·488) =	8·36	8·95	− 0·59
Ag	7	(107·92	× 0·011	+ 0·488) =	11·81	10·57	+ 1·24
Au	7	(197·23	× 0·011	+ 0·488) =	18·76	19·33	− 0·57

In answer to the original question, then, as to why the specific gravity of copper is about nine times that of sodium, whereas the atomic weight is only about three times as great, it may be stated that for the members of the sodium group and for the copper group the ratio of weight of the solid state has changed from that which held for atomic weight, and further that for the purpose of solidification the copper group takes a valency or value of seven times that of the sodium group.

The case for the non-metals and allied elements is different. For the non-metals generally the same zero appears for both the atomic and solid states, and as a consequence the atomic volume for each member of a group of elements is approximately the same as—

Chlorine	26·6
Bromine	25
Iodine	25·6
Oxygen	14·3
Sulphur	15·4
Selenium	17·6
Nitrogen	15·6
Phosphorus	14·7
Arsenic	15·9

South-Western Polytechnic.—The Eleventh Annual Distribution of Prizes and Certificates to the students of the Evening Classes and Day College will take place at this Institute on Friday, March 13th, 1908, when the Lord Alverstone, G.C.M.G., Lord Chief Justice of England, will present the awards. The Chair will be taken at 8 o clock p.m., by W. Hayes Fisher, Esq., Chairman of the Governing Body. There will be a selection of orchestral music at 7.30 p.m., under the direction of Mr. Seymour Dicker, Head of the Music Section.

ON THE VOLUMETRIC ESTIMATION OF POTASSIUM AS THE COBALTI-NITRITE.

By W. A. DRUSHEL.

THE use of sodium cobalti-nitrite for the qualitative detection of potassium is well known, and its use as a quantitative reagent has been described by R. H. Adie and T. B. Wood (*Journ. Chem. Soc.*, lxxvii., 1076; Sutton's "Vol. Anal.," 9th Ed., p. 62), whose results are fairly accurate and favourably comparable with results obtained by the platinic chloride gravimetric method. In the process worked out by these investigators a solution of a potassium salt containing the equivalent of 0·5 per cent to 1 per cent of K_2O is acidified with acetic acid and precipitated by an excess of sodium cobalti-nitrite. The mixture is allowed to stand at least a few hours, preferably over night, and is then filtered through a perforated crucible fitted with an asbestos felt. The precipitate is washed with 10 per cent acetic acid. According to Sutton it is important that the precipitation should be made in a solution containing the equivalent of 0·5 per cent to 1 per cent of K_2O, since in solutions of lower concentration the precipitate comes down in a condition in which it is apt to run through the filter in washing. The precipitate is then decomposed by boiling in dilute sodium hydroxide, and the cobalt is removed as the hydroxide by filtration. The nitrites, which are a measure of the potassium in the precipitate, are estimated by titrating with standard potassium permanganate. Adie and Wood found by analysis that the composition of the precipitated potassium salt is represented by the formula $K_2NaCo(NO_2)_6{\cdot}H_2O$. According to their method a cubic centimetre of strictly *n* 10 potassium permanganate is equivalent to 0·000785 grm. K_2O.

The object of this investigation was to determine the best conditions for precipitating and filtering the potassium cobalti-nitrite, and to shorten the work of estimating the potassium by oxidising directly with potassium permanganate without the preliminary decomposition of the precipitate and removal of cobalt recommended by Adie and Wood. In a series of preliminary experiments the precipitated cobalti-nitrite was oxidised by an excess of potassium permanganate, the excess of permanganate reduced by standard oxalic acid, and the remaining oxalic acid titrated to colour. In this treatment trivalent cobalt is reduced to the bivalent condition, and from the formula of potassium sodium cobalti-nitrite it would appear that the oxygen thus made available should be equivalent to one-twelfth of that necessary to oxidise the nitrites. The results of these experiments are given in Table I.

TABLE I.

No.	K_2O taken.	$KMnO_4$ used in titration of nitrites after removal of cobaltic hydroxide.	$KMnO_4$ equivalent to cobaltic hydroxide.	$KMnO_4$ used in direct titration.
	Grm.	Cc.	Cc.	Cc.
1.	0·0235	32·4	2·5	—
2.	0·0235	32·25	2·5	—
3.	0·0235	32·65	2·55	—
4.	0·0353	48·35	3·88	—
5.	0·0353	49·00	3·95	—
6.	0·0235	—	—	30·00
7.	0·0235	—	—	29·65
8.	0·0235	—	—	29·4
9.	0·0353	—	—	43·65
10.	0·0353	—	—	44·4

Portions of a potassium chloride solution of known strength were treated with an excess of sodium cobalti-nitrite and filtered on perforated crucibles fitted with asbestos felts. (The sodium cobalti-nitrite was prepared according to the directions given by Adie and Wood, *loc. cit.*, also given in Sutton's "Volumetric Analysis," 9th Ed., p. 62). The precipitates were first washed with

a 10 per cent acetic acid solution, then once with water. In Experiments 1 to 5 the precipitate was decomposed by boiling with sodium hydroxide and the nitrites estimated according to the method of Adie and Wood, giving the results in the second column of Table I. The cobaltic hydroxide filtered off on asbestos was reduced by heating nearly to boiling in a measured amount of standard oxalic acid containing a little sulphuric acid. The excess of oxalic acid was estimated by titrating with standard potassium permanganate, and from this the equivalent of the cobaltic hydroxide in terms of permanganate was found by subtraction, giving the results in the third column of the table. In Experiments 6 to 10 the precipitated potassium salt together with the crucible and asbestos felt, after stirring the precipitate and felt loose from the crucible, was placed in a beaker containing a measured amount of standard permanganate, taking care to use an excess, diluted to about ten times its volume, and heated nearly to boiling. After five to eight minutes, or when the manganese hydroxide formed gave the solution a dark colour, it was acidified with 5 cc. to 20 cc. of sulphuric acid (1 : 7). After a few minutes a measured excess of standard oxalic acid was run in from a burette, the temperature being kept a little below the boiling-point until the solution became clear, and then titrated to colour with permanganate. The whole amount of permanganate used less the equivalent of the oxalic acid used is the amount necessary for the oxidation of the precipitate. The results are given in the fourth column.

From the results of Table I. it appears that the oxidising value of the cobaltic hydroxide in terms of permanganate is nearly one-twelfth of that required for the oxidation of the nitrites, while the amount of permanganate necessary in the presence of the cobalt is nearly eleven-twelfths of that required for the oxidation of the nitrites after the removal of the cobalt. The factor used, therefore, in calculating the results from the direct titration should be twelve-elevenths of that given by Adie and Wood; that is, in titrating the precipitate without first separating the cobalt one cubic centimetre of strictly *n*/10 potassium permanganate is equivalent to 0·000856 grm. K_2O.

Unless the potassium salt solution is of the proper concentration the precipitate is very difficult to filter and wash, and shows a tendency to pass through the felt. By repeated experiments it was found that this difficulty, as well as the necessity for allowing the precipitate to stand over night, is avoided by evaporating the mixture nearly to dryness on the steam bath after adding the sodium cobalti-nitrite solution in considerable excess. Upon cooling the pasty residue it becomes hard and dry. It is then treated with cold water to dissolve the excess of sodium cobalti-nitrite, and the insoluble portion is collected on the filter. This precipitate may be freely washed with cold water without showing a tendency to pass through the filter, and is so insoluble that less than 0·5 of a mgrm. of the dried precipitate will dissolve in a litre of water at the room temperature during twenty-four hours standing with occasional shaking. This mode of treatment was found to work well and was used in all the subsequent experiments.

The method as worked out and used in all the experiments except those of Table I. is as follows:—The solution of a potassium salt, containing not more than 0·2 grm. K_2O and free from ammonium salt, was treated with a rather large excess of sodium cobalti-nitrite solution acidified with acetic acid, and evaporated to a pasty condition over the steam bath. It was then cooled and treated with 50 cc. to 100 cc. of cold water, and stirred until the excess of sodium cobalti-nitrite was dissolved. It was allowed to settle and decanted through a perforated crucible fitted with an asbestos felt. The precipitate was washed two or three times by decantation, after which it was transferred to the crucible and thoroughly washed with cold water. In the meantime a measured excess of standard potassium permanganate was diluted to ten times its volume and heated nearly to boiling. Into this the precipitate and felt were transferred and stirred up, after which the crucible was also put into the solution, since particles of the precipitate stick persistently to the sides of the crucible. After the oxidation had proceeded five or six minutes manganese hydroxide separated out and the colour of the solution darkened. At this point 5 cc. to 25 cc. of sulphuric acid (1 : 7) were added, and the solution, after stirring, was allowed to stand a few minutes. Then a measured amount of standard oxalic acid, containing 50 cc. strong sulphuric acid per litre, was run in from a burette, taking care to add an excess. The temperature was maintained a little below the boiling-point until the solution became colourless and the manganese hydroxide had completely dissolved. It was then titrated to colour by permanganate in the usual manner. From the whole amount of permanganate used the permanganate equivalent of the oxalic acid used was subtracted and the remainder multiplied by the factor calculated for the strength of permanganate used, 0·000856 being the factor for strictly *n*/10 potassium permanganate.

To make the *n* 10 oxalic acid solution, exactly 7·1066 grms. of pure recrystallised ammonium oxalate were dissolved in about 700 cc. of cold distilled water contained in a litre flask. To this solution were then added 50 cc. of strong sulphuric acid. The contents of the flask were cooled to 15° C. and made up to the mark with distilled water. The potassium permanganate solution was made approximately decinormal and standardised in the usual way. This standard was checked by standardising under conditions as nearly as possible like those under which the solution was used. A measured portion was diluted ten times, heated nearly to boiling, acidified with dilute sulphuric acid, and allowed to stand a few minutes. It was then bleached with a measured amount of oxalic acid, using it in slight excess, and titrated to colour. The two methods agreed very well, the difference in permanganate seldom being greater than one-tenth to two-tenths of a cubic centimetre in 25 cc.

Table II.

No.	K_2O taken. As KCl.	K_2O found. Gravimetrically.	K_2O found. Volumetrically.	Error in K_2O. Gravimetrically.	Error in K_2O. Volumetrically.
	Grm.	Grm.	Grm.	Grm.	Grm.
1.	0·0237	0·0240	0·0238	+0·0003	+0·0001
2.	0·0237	0·0243	0·0242	+0·0006	+0·0005
3.	0·0354	0·0359	0·0355	+0·0004	—
4.	0·0474	0·0478	0·0471	+0·0004	−0·0003
5.	0·0048	0·0048	0·0050	—	+0·0002
6.	0·0024	0·0024	0·0023	—	−0·0001
7.	0·0005	—	0·0006	—	+0·0001
8.	0·0015	—	0·0017	—	+0·0002
9.	0·0355	—	0·0355	—	—

In the first six experiments of this series the precipitate was dried at 115° C. and weighed. It was then treated with permanganate by the method previously described. Experiments 6, 7, and 8 show that very small amounts of potassium may be estimated with a fair degree of accuracy.

In Table III. the effect of the presence of members of the calcium group was investigated. Calcium and magnesium apparently do not interfere, while barium and strontium tend to give high results.

Table III.

	$CaCl_2$ taken.	$MgCl_2$ taken.	$BaCl_2$ taken.	$Sr(NO_3)_2$ taken.	K_2O taken.	K_2O found.	Error.
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
1.	0·2000	0·2000	—	—	0·0005	0·0007	+0·0002
2.	0·3000	0·5000	—	—	0·0237	0·0234	−0·0003
3.	0·5000	1·0000	—	—	0·0829	0·0824	−0·0005
4.	0·5000	1·0000	—	0·5000	0·0711	0·0737	+0·0026
5.	0·5000	1·0000	0·5000	0·5000	0·0474	0·0493	+0·0019
6.	0·5000	1·0000	0·5000	—	0·0237	0·0251	+0·0014
7.	0·5000	1·0000	—	—	0·0711	0·0713	+0·0002

The method may also be used in the presence of phosphoric acid and is therefore applicable to the estimation of K_2O in fertilisers. In Table IV. are the results obtained in nine fertilisers by the platinic chloride method and the cobalti-nitrite volumetric method. In columns one and two are the duplicate results obtained by two analysts of the Connecticut Agricultural Experiment Station, and in column three are the results by the volumetric method. The water-soluble phosphoric acid present in these samples is given in the fourth column.

TABLE IV.

Per cent K_2O in mixed fertilisers.

No.	K_2O by platinum chloride method.		K_2O by volumetric cobalti-nitrite method.	Per cent water-soluble P_2O_5 in sample.
1.	5·22	5·18	5·18	4·16
2.	6·53	6·56	6·56	3·10
3.	2·23	2·24	2·24	7·82
4.	8·68	8·64	8·78	0·94
5.	6·37	6·42	6·38	6·62
6.	6·08	6·13	6·13	5·61
7.	4·08	4·02	4·02	3·15
8.	4·62	4·66	4·67	2·43
9.	1·68	1·67	1·77	6 03

Ten grms. of the fertiliser were placed in a 500 cc. flask and 300 cc. of water were added. The contents were boiled for thirty minutes and ammonia water was added to slight alkalinity. Enough ammonium oxalate was added to precipitate all the calcium, and, after cooling, the solution was made up to the mark on the neck of the flask and well shaken. The solution was then filtered through a dry filter into a dry flask. Two 50 cc. portions of the filtrate were transferred with a pipette to platinum dishes, one portion being used for the gravimetric estimation by the platinum chloride method and the other for the volumetric estimation by the cobalti-nitrite method. After evaporating these portions to half their volume over the steam-bath, 1 cc. sulphuric acid (1 : 1) was added and the evaporation was continued as far as possible over the steam-bath, and finally over a low flame. After the danger of spattering was over the flame was increased and the charred organic matter was burned off, finally, over the blast lamp. The potassium sulphate was dissolved by adding a little water and heating over the steam-bath, and the potassium was estimated as previously described.

The volumetric method may be summed up thus: The potassium is precipitated as potassium sodium cobalti-nitrite by an excess of sodium cobalti-nitrite and the mixture is evaporated on the steam-bath. The precipitate is separated by filtration through asbestos and oxidised by hot standard potassium permanganate. The excess of permanganate is bleached by an excess of standard oxalic acid, and the solution is then titrated to colour by permanganate. The amount of potassium oxide is found by multiplying the oxygen value of the amount of potassium permanganate used by the factor 1·09.

This method has the advantages over the platinum chloride method, that no expensive reagents are used and that the time required for a determination is materially reduced. The method is considerably shorter than that of Adie and Wood and does not require the potassium solution to be of any definite concentration to work well.

In closing, the author desires to acknowledge his indebtedness to Dr. R. G. Van Name for many helpful suggestions during the progress of the work.—*American Journal of Science*, xxiv., p. 433.

Faraday Society.—Sir Oliver Lodge will deliver his Presidential Address to the Society on Tuesday, March 24th, next. The subject of the Address will be "Some Aspects of the Work of Lord Kelvin."

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

Ordinary Meeting, February 20th, 1908.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

THE PRESIDENT announced that letters have been received from those gentlemen recently elected Honorary and Foreign Members, acknowledging the honour which the Society desired to pay them.

Certificates were read for the first time in favour of Messrs. Albert Edward Findley, B.Sc., 1, Welford Road, Handsworth, Birmingham; George Edward Holden, 23, Durnford Street, Middleton, Manchester; Percy Hulme Hornby, 111, Nine Elms Lane, S.W.; Herbert Mansfield, B.Sc., A.I.C., 70, Stapleton Hall Road, Stroud Green, N.

Certificates have been authorised by the Council under Bye-Law I. (3) in favour of Messrs. Bidhu Bhushan Dutt, M.A., Presidency College, Calcutta; Atul Chandra Gañguli, B.A., Ravenshaw College, Cuttack, India; Arthur Horrobin, Ajmer, Rajputana, India; Pañchanan Neogi, Rajshahi College, Rajshahi, Bengal.

It was announced that the following changes in the Officers and Council were proposed by the Council:—

Vice-Presidents to retire—Prof. A. Smithells and Prof. W. P. Wynne.

Ordinary Members of Council to retire—Mr. E. C. C. Baly, Dr. Bernard Dyer, Mr. E. Grant Hooper, and Dr. G. T. Moody.

As President—Sir William Ramsay.

As Vice-Presidents who have filled the office of President—Prof. H. E. Armstrong, Prof. A. Crum Brown, Sir William Crookes, Sir James Dewar, Dr. A. G. Vernon Harcourt, Prof. R. Meldola, Dr. H. Müller, Prof. W. Odling, Prof. J. Emerson Reynolds, Sir Henry E. Roscoe, Dr. W. J. Russell, Prof. T. E. Thorpe, and Prof. W. A. Tilden.

As Treasurer—Dr. Alexander Scott.

As Secretaries—Dr. M. O. Forster and Prof. A. W. Crossley.

As Foreign Secretary—Dr. Horace T. Brown.

As Vice-Presidents—Prof. J. Campbell Brown, Prof. J. J. Dobbie, Prof. F. S. Kipping, Dr. R. Messel, Sir A. Pedler, and Prof. W. H. Perkin.

As New Ordinary Members of Council—Mr. J. L. Baker, Mr. A. C. Chapman, Prof. J. B. Cohen, and Dr. J. T. Hewitt.

Dr. A. Harden, Dr. H. Forster Morley, and Dr. J. A. Voelcker were elected Auditors to audit the Society's Accounts.

A ballot for the election of Fellows was held, and the following were subsequently declared elected:—Edward Philip Andreae, Ph.D.; Guy Barr, B.A., B.Sc.; Robert Barton, jun.; Marie Joseph Arsène Braun, Ph.D.; Harry James Brown; Walter Brown, jun.; John Arthur Carpenter, B.A.; Hans Thacher Clarke; Archibald Edgar Collens; William Henry Collier; David Cowan Crichton, M.A., B.Sc.; Cyril Dickinson, B.Sc.; Edwin Mortimer Eagles, M.A.; Joseph Valentine Francies; Robert Cecil Gale; John Maxwell Heron; Thomas Percy Hilditch; Arnold Merrick; Capel Darcy Morewood; Alfred William Oke, B.A., LL.M.; George Neville Pingriff, B.A.; Douglas Robert Pinnock; Arthur Robert Runeckles; Andrew L. Scott; William Bayliss Shaw; Puran Singh; John Armstrong Smythe; Charles Sedgley Spiers; Arthur Stead, B.Sc.; Adolph Octavius Trechmann; Thomas Marshall Tyson; Harry Jackson Unwin; Alfred Wade; Herbert Walker; Herbert Edmeston Watson, B.Sc.; John Watson, B.Sc.; David Thomas Williams; Joseph Henry Williams; Harry Percy Wilson; William Henry Withey, B.A.; Francis Charles Benjamin Wood; Joseph Yates.

Of the following papers, those marked * were read:—

*32. "*Organic Derivatives of Silicon.* Part VI. *The Optically Active Sulphobenzylethylpropylsilicyl Oxides.*" By Frederic Stanley Kipping.

The sulphonic acids obtained by resolving *dl*-sulphobenzylethylpropylsilicyl oxide with one of the active methylhydrindamines (*Trans.*, 1907, xci., 209) have been further studied, and the results clearly show that the two acids are optically active, enantiomorphously related compounds having the constitution $(SO_3H{\cdot}CH_2{\cdot}C_6H_4{\cdot}SiEtPr)_2O$; although they contain two asymmetric silicon groups, their specific rotations are very small, the values obtained for the sodium salts being $[\alpha]_D \pm 5{\cdot}8—5{\cdot}9°$.

The crystalline *dA*d*B*- and *l*A*l*B-methylhydrindamine derivatives differ very widely in outward properties from the *dA*l*B*- and *l*A*d*B- compounds, which have a very gelatinous or horny nature, but all four salts have a specific rotation $[\alpha]_D \pm 15—16°$ in methyl-alcoholic solution.

The *dA*l*B*- and *l*A*l*B-menthylamine salts are practically indistinguishable from one another or from the salt of the *dl*-acid, and this is also true in the case of the corresponding three *d*-bornylamine derivatives; the cinchonidine and cinchonidine hydrogen salts of the two active acids differ slightly in melting point.

dl-Sulphobenzylethylpropylsilicyl oxide is decomposed by hot concentrated sodium hydroxide, giving *p*-toluenesulphonic acid.

*33. "*The Preparation of Conductivity Water.*" By Harold Hartley, Norman Phillips Campbell, and Reginald Holliday Poole.

The efficiency of different methods of preparing conductivity water has been investigated in order to find a trustworthy way of obtaining water with a specific conductivity not greater than 1 gemmho ($1{\cdot}0 \times 10^{-6}$ reciprocal ohms) in a chemical laboratory under ordinary conditions. By combining several devices in use in other laboratories, a still has been constructed which in one operation gives a fair yield of water with a conductivity of 0·75 gemmho at 18°, starting from ordinary distilled water with a conductivity of 5 gemmhos without any preliminary chemical treatment. The distillation can be carried out in a chemical laboratory where nothing is done to keep the air specially free from impurities.

Discussion.

Dr. T. M. Lowry congratulated the authors on being able to produce water of such low conductivity under ordinary laboratory conditions. The still described by Mr. Bousfield (*Trans.*, 1905, lxxxvii., 740) gave almost equally good water (after boiling in a platinum flask, values as low as 0·45 gemmho had been obtained), and had the advantage that it could be left running without attention for a month at a time, but the quality of the water deteriorated when the still was worked in an impure atmosphere, unless special precautions were taken to protect the distillate. It was now generally recognised that the air rather than glass or metal vessels was the most dangerous source of contamination; "gemmho" water could be stored for many months without deterioration in the large green bottles in which the Welsbach solutions were imported, and which could be purchased through the ordinary trade channels; on the other hand, water of lower conductivity did not usually repay the trouble involved in its preparation, since it deteriorated so rapidly in contact with air that it was likely (by giving a false impression of its actual purity) to introduce rather than eliminate an error in conductivity measurements.

Dr. Philip asked whether, in view of the fact that a Jena glass flask was found suitable for storing the pure water, the metal parts of the condenser might not be replaced by Jena glass apparatus.

In answer to Dr. Philip, Mr. Hartley said that very good results had been obtained with a Jena glass condenser, but a block tin tube was better, as it produced more rapid condensation, and could be soldered into the condensing vessel, avoiding the use of corks which required frequent renewal.

*34. "*Derivatives of Para-diazoiminobenzene.*" By Gilbert Thomas Morgan and Francis Mary Gore Micklethwait.

It has been shown that the explosive diazoimino-derivative obtained by Hantzsch from phenyl-*p*-phenylenediamine (*Ber.*, 1902, xxxv., 895) belongs to the same group of compounds as the stable arylsulphonyl-*p*-diazoimides prepared by the authors. A series of substances connecting this unstable *p*-diazoimine with the *p*-diazoimides has been obtained by a study of the diazo-derivatives of 2 : 4 : 6-trinitrophenyl-*p*-phenylenediamine, 2 : 4-dinitrophenyl-*p*-phenylenediamine, 4-nitrophenyl-*p*-phenylenediamine, and 2-nitrophenyl-*p*-phenylenediamine.

The first of these bases, which contains a substituent comparable in acidic character to the acyl groups in the arylsulphonyl-*p*-diamines, furnishes a stable *p*-diazoimino-derivative similar in its properties to the arylsulphonyl-*p*-diazoimides, and produced under comparable conditions by the action of sodium acetate on the diazo-salt of 2 : 4 : 6-trinitrophenyl-*p*-phenylenediamine.

The diazo-salts of 2 : 4-dinitrodiphenyl-*p* phenylenediamine give rise to a diazoimine only when treated with potassium hydrogen carbonate, but not with aqueous sodium acetate. The product is more explosive than the trinitro-derivative.

The diazo-salts of 2- and 4-nitrophenyl-*p*-phenylenediamine do not yield diazoimines either with an alkali acetate or carbonate, but only on treatment with ammonia is the condensation product obtained. In this respect, these bases behave like phenyl-*p*-phenylenediamine itself.

These results show that the ease of formation and the stability of the derivatives of the hypothetical *p*-diazoiminobenzene are determined by the acidic nature of a substituent attached to one aminic nitrogen.

Discussion.

Dr. George Young pointed out that five-atom carbon-nitrogen rings differ markedly in their nature, and especially in regard to their stability, from heterocyclic nuclei containing either a greater or smaller number of atoms in the ring. Hence arguments based on a comparison of the *p*-diazoiminobenzenes with compounds such as *o*-diazoiminobenzene or Wolff's derivative of tetronic acid, which contain five-atom rings, cannot be decisive as between the benzenoid constitution discussed by Dr. Morgan, in which there is a seven-atom and the quinonoid formula with its three-atom heterocyclic grouping.

Dr. Morgan, in reply to Dr. Hewitt, said that in conjunction with Mr. E. G. Couzens he had made many attempts to prepare diazoimides of the meta-series from the benzenesulphonyl-*m*-diamines of benzene, toluene, *m*-xylene, and mesitylene. Being entirely unsuccessful, they inferred that the diazoimide condensation was not wholly a matter of internal salt formation, and that the change occurred only when this factor was reinforced by the tendency for ring formation which characterises the ortho- and para-derivatives as distinguished from the meta-series. The picryl-*p*-phenylenediazoimine closely resembled the para-diazoimides, and it seemed only reasonable to suppose this compound also owed its existence to the combined operation of these salt and ring-forming tendencies.

With regard to the point raised by Dr. Cain in reference to the validity of analogies concerning the constitution of ortho-, para-, and peri-derivatives based on experimental evidence obtained from the last of these three series, it seemed to him that this testimony was greatly to be preferred to that derived from a comparison instituted between substances so very dissimilar as *p*-aminophenol and *a*-aminotetronic acid.

*35. "*The Affinity Constants of Bases as Determined by the Aid of Methyl-orange.*" By Victor Herbert Veley.

The author has extended the work of which a pre-

liminary account has already appeared (*Proc.*, 1907, xxiii., 284).

Results were given for the hydrochlorides of (i.) bases not containing an alkyl grouping; (ii.) aliphatic amines; (iii.) aminoacetic acids; and (iv.) uric acid derivatives. As regards hydrazine in (i.), and all cases of (iii.), it was shown that the results obtained by the methyl-orange method are concordant with those obtained by the electric conductivity method, although the dilutions were about forty to eighty times greater. The tentative conclusion was drawn that either there is a limiting value of V in the Arrhenius equation $K_h K_w = (1-x)V/x^2$, or that the hydrolytic reaction becomes reversible. As regards cases of (iv.), the general agreement of the results obtained by the methyl-orange method with those of the solubility method was considered, although the increase of hydrolysis relative to dilution is less than that required by Arrhenius' formula.

36. "*The Action of Thionyl Chloride and of Phosphorus Pentachloride on the Methylene Ethers of Catechol Derivatives.*" By George Barger.

In the chloro-compounds, formed by heating the methylene ethers of catechol derivatives with phosphorus pentachloride, the most labile chlorine atoms are those introduced into the methylene group. By the action of water or of glacial acetic acid at low temperatures, this pair of chlorine atoms is replaced by an oxygen atom, with the formation of a cyclic carbonate. The "dichlorpiperonal" of Fittig and Remsen (*Annalen*, 1871, clix., 144) is therefore the cyclic carbonate of 3:4-dihydroxybenzylidene chloride (I.), and does not possess an aldehyde group as implied by the present formula (II).

$$O{:}C{<}^{O}_{O}{>}C_6H_3{\cdot}CHCl_2. \qquad Cl_2{:}C{<}^{O}_{O}{>}C_6H_3{\cdot}CHO.$$

I. II.

Similarly, the supposed chloro-acid, obtained by Fittig and Remsen from piperonylic acid in an impure condition, is in reality the cyclic carbonate of protocatechuoyl chloride or carbonyldioxybenzoyl chloride, $O{:}C{:}O_2{:}C_6H_3{\cdot}COCl$.

Heating with excess of thionyl chloride to 180° has the same effect as phosphorus pentachloride and water, so that cyclic carbonates are formed directly from the methylene ethers.

3:4-*Carbonyldioxybenzoyl chloride* boils at 166—167°/12 mm., and crystallises from a mixture of benzene and light petroleum in stout crystals melting at 68°. Several derivatives were described.

37. "*A Study of the Diazo-reaction in the Diphenyl Series.*" By Gilbert Thomas Morgan and Francis Mary Gore Micklethwait.

The arylsulphonylbenzidines, $RSO_2{\cdot}NH{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2$, furnish yellow, crystalline diazonium salts giving rise, on treatment with aqueous sodium acetate, to dark brown crystalline compounds which are either monohydrated nitrosoamines, $R{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH{\cdot}NO,H_2O$, or dihydrated diazoimides (I.):—

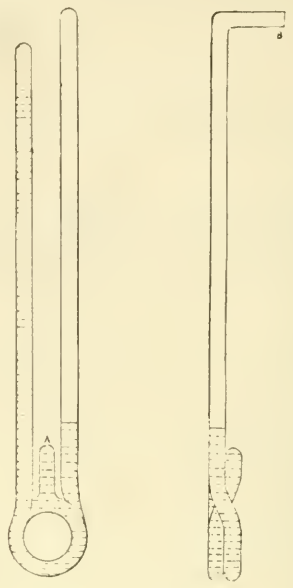
$$\begin{matrix} C_6H_4{\cdot}N_2 \\ | \quad | \\ C_6H_4{\cdot}N{\cdot}SO_2R,2H_2O \end{matrix} \qquad \begin{matrix} C_6H_4{\cdot}N_2 \\ | \quad | \\ C_6H_4{\cdot}NH \end{matrix}$$

I. II.

In this respect, these acylbenzidines differ from benzidine, which gives rise to a diazoimide (II.). The diazonium salts of the arylsulphonylalkylbenzidines, $RSO_2{\cdot}N(C_2H_5){\cdot}C_6H_4{\cdot}C_6H_4{\cdot}NH_2$, although distinctly less coloured than those of the unalkylated bases, have nevertheless not been obtained in a colourless condition. There is accordingly no reason for supposing that the diazonium salts of the alkylated bases are differently constituted from those which still contain the labile acidic hydrogen atom (*).

38. "*A Simple Manometer for Vacuum Distillation.*" By Norman Leslie Gebhard.

The manometer described consists essentially of a barometer tube bent in the form depicted in the figure. The simple trap A prevents effectually any air from being forced back into the barometer tube and thus affecting the readings. In order to remove any air thus trapped, it is merely necessary to incline the apparatus so that the



mercury expels the air into the open arm again; this is, however, only necessary at the end of an operation, as the apparatus is capable of yielding accurate readings in spite of the presence of air in the trap.

39. "*Researches on the Anthraquinones.*" By William Henry Bentley and Charles Weizmann.

An account was given of the condensations of: (1) phthalic anhydride and pyrogallol trimethyl ether; (2) hemipinic anhydride and veratrole; (3) hemipinic anhydride and pyrogallol trimethyl ether in presence of aluminium chloride. These reactions yield respectively: (1) *trimethoxybenzoylbenzoic acid*, m. p. 169°; (2) *tetramethoxybenzoylbenzoic acid*, m. p. 193—194°; (3) *hydroxytetramethoxybenzoylbenzoic acid*, m. p. 190°. These acids on further condensation with concentrated sulphuric acid yield respectively: (1) *dihydroxymonomethoxyanthraquinone*, m. p. 235—236°; (2) *hydroxytrimethoxyanthraquinone*, m. p. 226°; (3) *trihydroxydimethoxyanthraquinone*, m. p. 230°. By employing phosphoric oxide in place of sulphuric acid, it was found possible to obtain tetramethoxyanthraquinone (m. p. 239°) from tetramethoxybenzoylbenzoic acid.

40. "*The Formation of 4-Pyrone Compounds from Acetylenic Acids.*" Part I. By Siegfried Ruhemann.

The author finds that ethyl phenylpropiolate condenses with the ketones of formula $R{\cdot}CH_2{\cdot}CO{\cdot}R'$ in presence of sodium ethoxide to form 4-pyrone derivatives thus:—

$$C_6H_5{\cdot}C{:}C{\cdot}CO_2Et + CH_2{\cdot}R{\cdot}CO{\cdot}R' = C_6H_5{\cdot}C{\equiv}\begin{matrix}CH{\cdot}CO\\O{-}CR'\end{matrix}{\geq}C{\cdot}R + C_2H_6O.$$

Up to the present, acetone and acetophenone have been used, and 2-phenyl-6-methyl-4-pyrone,—

$$C_6H_5{\cdot}C{\equiv}\begin{matrix}CH{-}{-}CO\\O{\cdot}C(CH_3)\end{matrix}{\geq}CH,$$

and 2:6-diphenyl-4-pyrone,—

$$C_6H_5{\cdot}C{\equiv}\begin{matrix}CH{-}{-}CO\\O{\cdot}C(C_6H_5)\end{matrix}{\geq}CH,$$

respectively have been obtained.

Along with diphenyl-4-pyrone, there is formed in this reaction a colourless compound, $C_{25}H_{20}O_3$, which yields a violet solution with concentrated sulphuric acid, and is produced according to the equation $C_6H_5{\cdot}C{\vdots}C{\cdot}CO_2Et + 2C_6H_5{\cdot}CO{\cdot}CH_3 = C_{25}H_{20}O_3 + C_2H_6O$.

$C_6H_5{\cdot}CH_2{\cdot}CO{\cdot}CO{\cdot}C(CO{\cdot}C_6H_5){:}C(CH_3){\cdot}C_6H_5$ is the formula suggested for this substance.

41. "*The Action of Mustard Oils on the Ethyl Esters of Malonic and Cyanoacetic Acids.*" By Siegfried Ruhemann.

Ethyl sodiomalonate reacts with phenyl thiocarbimide, thus :—

$$CHNa(CO_2Et)_2 + C_6H_5{\cdot}NCS = C_6H_5{\cdot}N{:}C(SNa)CH(CO_2Et)_2,$$

and this additive product, with acids, yields diethyl thiocarbanilinomalonate, $C_6H_5{\cdot}NH{\cdot}CS{\cdot}CH(CO_2Et)_2$. This, on hydrolysis with dilute caustic potash, loses 1 molecule of carbon dioxide, forming *thiocarbanilinoacetic acid*, $C_6H_5{\cdot}NH{\cdot}CS{\cdot}CH_2{\cdot}CO_2H$, which melts at 91—92°, and at the same time evolves carbon dioxide to yield thioacetanilide. The colourless sodium compound of diethyl thiocarbanilinomalonate forms a *benzyl* derivative, which is also colourless, and has the formula $C_6H_5{\cdot}N{:}C(S{\cdot}CH_2{\cdot}C_6H_5){\cdot}CH(CO_2Et)_2$.

Ethyl sodiobenzylmalonate and phenyl thiocarbimide do not yeld a compound of formula $C_6H_5{\cdot}N{:}C(SH){\cdot}C(CH_2{\cdot}C_6H_5)(CO_2Et)_2$. This fact would point to a different way of representing the product of the union between ethyl sodiomalonate and phenyl thiocarbimide, but, for the present, the author adheres to the former view.

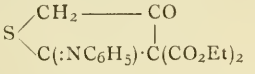
Ethyl sodiocyanoacetate also combines with phenyl thiocarbimide, and furnishes *ethyl thiocarbanilinocyanoacetate*, $C_6H_5{\cdot}NH{\cdot}CS{\cdot}CH(CN){\cdot}CO_2Et$. This compound is colourless, as are its *sodium* and *ammonium* salts as well as its *benzyl* derivative, $C_6H_5{\cdot}N{:}C(S{\cdot}CH_2{\cdot}C_6H_5){\cdot}CH(CN){\cdot}CO_2Et$, but on drying at 100° or on crystallisation from hot solvents it turns yellow. This behaviour is regarded as pointing to the existence of the substance in two tautomeric forms :—

$$C_6H_5{\cdot}N{:}C(SH){\cdot}CH(CN){\cdot}CO_2Et$$

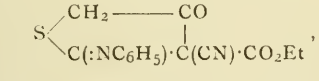
and—

$$C_6H_5{\cdot}NH{\cdot}CS{\cdot}CH(CN){\cdot}CO_2Et,$$

The action of ethyl chloroacetate on the sodium derivatives of diethyl thiocarbanilinomalonate and of ethyl thiocarbanilinocyanoacetate yields the *cyclic* compounds :—



and—



respectively ; these are yellow, but, under the influence of potassium hydroxide, change into colourless isomerides. The nature of these transformations is still under examination.

42. "*The Triazo-group.* Part II. *Azoimides of Propionic Ester and of Methyl Ethyl Ketone.*" By Martin Onslow Forster and Hans Eduard Fierz.

On comparing the behaviour of the α- and β-triazo-derivatives of ethyl propionate towards alkali, it was found that, whilst the first-named resembled triazoacetic ester, ethyl β-triazopropionate rapidly parts with hydrazoic acid.

α-Triazopropionic acid, $CH_3{\cdot}CHN_3{\cdot}CO_2H$, is a colourless oil, having a rancid odour, and forms crystals which melt at 0° ; the *silver* salt, $C_3H_4O_2N_3Ag$, crystallises from hot water in lustrous needles. The *ethyl* ester, $C_5H_9O_2N_3$, prepared from ethyl α-bromopropionate and sodium azide, boils at 46° under 2 mm. pressure, and has sp. gr. 1·065 compared with water at 23° ; the *amide*, $C_3H_6ON_4$, crystallises from benzene in rectangular plates, melting at 79°.

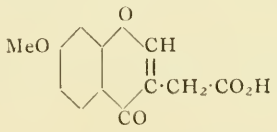
Ethyl-β-triazopropionate, $N_3{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2{\cdot}C_2H_5$, prepared from the iodo-ester and sodium azide, boils at 58° under 4 mm. pressure ; aqueous ammonia eliminating hydrazoic acid, it has not been possible to prepare the amide and the free acid from this ester.

3-Triazobutanone-2, $CH_3{\cdot}CO{\cdot}CHN_3{\cdot}CH_3$, produced on agitating the corresponding chloro-derivative of methyl ethyl ketone with aqueous sodium azide, boils at 46° under 2 mm. pressure, and has sp. gr. 1·057 at 18° ; the *semicarbazone*, $C_5H_{10}ON_6$, crystallises in snow-white plates, and melts at 94°.

1-Triazobutanone-2, $N_3{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_3$, boils at 56° under 2 mm. pressure, and has sp. gr. 1·084 at 18° ; it resembles the foregoing ketone and acetonylazoimide in its behaviour towards alkali and sulphuric acid. The *semicarbazone*, $C_5H_{10}ON_6$, crystallises in needles, and melts at 101°.

43. *Brazilin and Hæmatoxylin.* Part VIII. *Synthesis of Brazilinic Acid, the Lactones of Dihydrobrazilinic and Dihydrohæmatoxylinic Acids, Anhydrobrazilic Acid, &c. The Constitution of Brazilin, Hæmatoxylin, and their Derivatives.*" By William Henry Perkin, jun., and Robert Robinson.

The authors have continued and elaborated the work of which a preliminary account has already appeared (*Proc.*, 1907, xxiii., 291). Further confirmation of the constitution of the members of this group is afforded by the synthesis of *anhydrobrazilic acid*, which has been proved to possess the formula :—



PHYSICAL SOCIETY.

Ordinary Meeting February 28th, 1908.

Dr. Charles Chree, F.R.S., President, in the Chair.

A paper by Mr. S. W. J. Smith and Mr. H. Moss, entitled "*On the Contact Potential Differences determined by means of Null Solutions*," was read by Mr. Smith.

When a mercury jet breaks in the surface of an electrolyte there is in general an E.M.F. between the jet and a still mercury electrode immersed in the electrolyte. If the contact potential difference between the still mercury and the solution is π_s, that between the jet and the solution being π_d, the observed E.M.F. is $E_p = \pi_s - \pi_d$. This E.M.F. is found to be equal to the polarising E.M.F., E_m, required to produce the maximum surface-tension between mercury and the electrolyte.

Since $E_m = \pi_s - \pi_m$, where π_m is the potential difference between the Hg and the electrolyte when the surface-tension is a maximum, it follows that $\pi_m = \pi_d$. Apart from special assumptions nothing more concerning these potential differences can be deduced from the purely experimental result $E_m = E_p$.

From the latter it is seen that E_p can be predicted if E_m is known. If $E_m = 0$ then $E_p = 0$. Hence a mercury jet will show no potential difference against still mercury when both are in contact with an electrolyte for which the "natural" surface-tension is also the maximum. A solution for which $E_p = 0$ is called by Palmaer a "null solution." Without observing the electro-capillary curve he found by trial two solutions for which $E_p = 0$. Although he concluded from his experiments that $\pi_s = \pi_d = 0$, it is clear that, without special assumptions, the only necessary conclusion is $\pi_s = \pi_d = \pi_m$.

The primary object of the paper is to show that in

general Palmaer's deduction is not only unnecessary but wrong.

If an experimental method can be found of obtaining from any electrolyte MX (for which E_m is positive) a solution for which $E_m = 0$, then it will be possible to obtain an indefinite number of null solutions. Such a method has been found. It consists in the addition to the electrolyte of a particular small quantity of M_2S (throughout the experiments M = Na or K, although it seems certain that the process could be generalised).

A number of null solutions were found, including one which gave results practically identical with those obtained by Palmaer. It is shown, however, that the potential difference Hg | null solution is a variable. For example, Hg | null KI can differ by about a quarter of a volt from Hg | null KCl, although in each case $\pi_s = \pi_m = \pi_d$.

The only assumption made in interpreting the results is that equal surface-tensions mean equal potential differences in those parts of the electro-capillary curves (of salts of K and Na of equal ionic concentration) which are of identical form. This assumption is admitted in all the theories that have been proposed.

Mr. S. Skinner congratulated the authors upon the accurate series of experiments which they had carrried out.

Dr. W. Watson expressed his interest in the paper, referring especially to the action of dissolved oxygen present in the solutions.

Mr. F. E. Smith referred to the fact that in the paper values for the contact potential difference were given to four places of decimals, and asked if any significance could be attached to the last two figures. He pointed out that the results obtained from drop electrodes were very different from those obtained by Billitzer using a different method. He asked if experiments had been made with jets of various sizes and under various pressures, and whether the form of the curves had been sufficiently studied.

Mr. Lewis asked if the authors had used other substances besides Na_2S, and if they had taken account of chemical actions which might take place at the electrodes.

Dr. Erskine Murray referred to experiments he had made some years ago on contact potential differences between metals in which the oxygen of the air behaved in a manner analogous to the dissolved oxygen in the author's solutions.

Mr. S. W. J. Smith, replying to Mr. F. E. Smith, said that Palmaer's value for the contact potential difference between mercury and *n*/10 KCl solution was quoted from his paper. With regard to Billitzer's views, they laboured for the present under the disadvantage that other observers had tried, but failed, to reproduce the effects which he describes. The form of the electro-capillary curve had been carefully studied. Van Laar had formulated a theory based upon the fact that the curve can be considered to consist within the limits of experimental error of portions of two parabolas. His interpretation of the significance of the point at which the curve changes from one parabola to the other had in reality no experimental support. The question of the character of the jet, amount of immersion, &c., had been carefully studied, and certain relations between the E.M.F. and the time of contact with the liquid had been arrived at. His (Mr. Smith's) point of view differed from that of Paschen in that he believed the experimental evidence to show that the E.M.F. between a Paschen electrode and an electrolyte was not in general zero. He cited a case in which apparently the potential difference between a Paschen jet and one electrolyte ($ZnSO_4$) differs by nearly half a volt from that between a Paschen jet and another electrolyte ($CuSO_4$). It was only when the electro-capillary maxima for two electrolytes were equal that the Paschen E.M.F.'s for the electrolytes were the same. An electro capillary maximum could not be obtained for $CuSO_4$ solution, probably because of deposition of copper on the mercury, just as a maximum could not be obtained from concentrated H_2SO_4 on account of the evolution of hydrogen. Paschen's experiments did not prove that the potential difference between an electroiyte and a mercury jet breaking in its surface is zero. It was possible that a certain fraction (in some cases the whole, *e.g.*, in null solutions) of the steady potential difference might arise practically instantaneously.

In reply to Mr. Lewis, Mr. Smith remarked that they used Na_2S because it was deducible from electro-motive data—in agreement with chemical—that the solubility of mercury sulphide was extremely small even compared with that of calomel. In reference to Mr. Lewis's suggestion that certain interactions might take place between the mercury, the dissolved salt, and the Na_2S independently of the oxygen, he said that although he had found that the amount of Na_2S required (in the way the experiments were performed) was not chemically equivalent to the amount of oxygen in solution, yet the amounts of Na_2S and oxygen were found to be roughly proportional to one another in experiments they had performed with the help of Mr. W. F. Higgins. He indicated to the meeting directions in which further experimental evidence was being sought. The electro-motive method of tracing minute chemical change was both delicate and simple.

A paper on "*An Experimental Examination of Gibbs' Theory of Surface Concentration regarded as the Basis of Adsorption, and its Application to the Theory of Dyeing*," was read by Mr. W. C. M. Lewis.

The object of the paper was to investigate experimentally Gibbs' theory of surface concentration; this concentrating of a solute in the surface-layer of a solution being dependent on variations in surface-tension. The following is a particular form of the more general equation, viz.:—

$$\Gamma = \frac{-c}{RT}\frac{d\sigma}{dc},$$

where Γ = the excess mass of solute per sq. cm. surface, c = the bulk concentration of the solution, T = the absolute temperature, R = the gas constant, and σ = the surface-tension. Assuming surface-tension effects to be the basis of adsorption, measurements were made of the various quantities in the above equation. The material at the surface of which adsorption took place consisted of a pure hydrocarbon oil. The material adsorbed was bile-salt in aqueous solutions of different concentrations. The interfacial tension σ was measured by the drop-pipette method, a curve being obtained showing the variation of tension with concentration. Γ was measured in two ways —(1) at the surface of oil-drops of radius about 1 mm., and (2) at the surface of drops of radius about 10^{-4} mm., *i.e.*, emulsion particles. Determinations by both methods agreed within the limits of experimental error. Similar experiments were made with certain dye-stuffs. The general result was that the actual values found for Γ exceeded the calculated by about fifty times the latter, the conclusion being that there is a real discrepancy of considerable magnitude. As regards the discrepancy noted, no suggestion is as yet offered, but the author stated that it might be connected with possible concentration changes at the surfaces.

Mr. S. W. J. Smith remarked with reference to the author's opinion that possible concentration changes at the surface of the mercury might have some bearing upon contact potentials, that Warburg had developed a theory of electro-capillarity based upon this assumption. It had been shown that mercury drops falling through a solution of a salt produced changes of concentration, just as in the author's experiments concentration changes were produced in a solution by rising drops of oil. There were at least two different interpretations of the mercury experiments.

Mr. A. Campbell asked if the absorption of moisture from the air by cellulose was a case of adsorption, and also if the amount of adsorption in dyeing depended upon the temperature.

Mr. Lewis said there was little doubt that the deposition of moisture on cellulose was a case of adsorption. Adsorption is accompanied by an evolution of heat, and a rise of temperature decreases adsorption.

SOCIETY OF CHEMICAL INDUSTRY.
(London Section).

Ordinary Meeting, March 2nd, 1908.

Dr. J. Lewkowitsch in the Chair.

The Honorary Secretary, Mr. Julian L. Baker, read an Obituary Account of the late Chairman, Mr. R. J. Friswell.

The Honorary Secretary then read the following paper, "*The Preparation of Para-Toluidine from Mixed Toluidines by Means of Para-Toluidine Hydrate*," by the late R. J. Friswell.

A paper has recently been published (*Trans. Chem. Soc.*, 1907, xci., 1797) by J. W. Walker and Miss Beveridge describing a hydrate of para-toluidine. The problem of preparing pure para-toluidine is of great importance in the coal-tar products industry, inasmuch as this base is the material employed in the production of the well-known colouring principle primuline, and is likewise a constituent of several other commercially valuable artificial colouring matters. This mixture of bases obtained by the reduction of the crude nitro-toluene contains 35 to 40 per cent of the more valuable para-toluidine, and this was separated by churning the crude product with small fragments of ice. The plant employed in this operation consisted of a machine with a rotating ice-breaker and a beater, which took the form of a covered-in cylindrical tank in which the ice and bases could be pounded together. A change in the sound produced by the stirrers showed when the reaction was complete, and the product, which had now the consistence of a stiff paste, was blown into a filter-press, and in this way a solid compound of para-toluidine and water was obtained and freed from ortho-toluidine, which, under these conditions, does not form a hydrate. The press-cakes of para-toluidine hydrate were then melted up and the base freed from water and distilled. In this way pure para-toluidine could be easily prepared at a moderate cost. This method was devised by the author in 1889, and since then large quantities of pure para-toluidine have been prepared by it.

"*The Chloramin Reactions of the Proteins, and Technical Applications.*" By C. F. Cross, E. J. Bevan, and J. F. Briggs.

Monochloramin, NH_2Cl, is formed by the interaction of ammonia and chlorine; more conveniently, and in fact quantitatively, by the interaction of ammonia and hypochlorites (F. Raschig, *Ber.*, 1907, xl., 4586). Reacting with a second molecule, hydrazine is synthesised, $NH_2ClNH_3 = H_2N{\cdot}NH_2HCl$, and this typical reaction has been extended to aromatic amines (*Zeit. Angew. Chem.*, 1907, xx., 2065).

The authors find that the amine groups of the nitrogenous colloids (proteins) react similarly, forming characteristic chloramines which are relatively stable. The combined chlorine reacts with hydriodic acid thus: $XNHCl + 2HI = XNH_2 + HCl + I_2$, and hence volumetric iodometric methods are available for estimating these chloramines.

Gelatin (hydrated) gives maximum and constant numbers by reaction with the pure halogen, fixing 9 per cent of its weight (dry) of chloramin Cl, equivalent therefore to 16 per cent "active Cl." On this is based a much simplified method of estimating gelatin in "tub-sized" papers. The gelatin chloramin, washed, dehydrated, and dried, has been kept ten weeks without the loss of "active chlorine."

The tissue proteins of flax react to form chloramins in the hypochlorite liquors of the linen bleacher. The chlorine fixed is proportional to the nitrogen contents of the flax in the successive stages of purification of the goods, yarns or fabrics. Thus fixed to form chloramins these resist "souring" and washing. Trade samples of "creamed" flax yarns have been found to contain as much as 0·1 per cent of such "active chlorine."

Hydrolysed chloramines are present in the standing "bleach liquors," and a method has been devised for their estimation, based on their differential resistance to hydrogen peroxide. They have the peculiar property of combining with cellulose in such a way as to resist washing. These results are of fundamental importance to the textile bleaching industry. The chloramin reaction is of service in histological investigations in localising proteins and amino compounds.

The nitrogenous colloids in reacting to form chloramins appear to retain their colloidal characteristics, and the results of these investigations promise to contribute to the solution of problems of the colloidal state, including those of dyeing and photographic action.

FARADAY SOCIETY.

Ordinary Meeting, February 25th, 1908.

Mr. T. M. Lowry in the Chair.

Dr. V. H. Veley, F.R.S., read a paper on "*Hydrolysis as Illustrated by Heats of Neutralisation.*"

In this paper it is pointed out that a correlation of hydrolysis values, and basic constants deduced therefrom, with those of heats of neutralisation, presents interesting and important issues. As regards the former, determinations at different temperatures by equally accurate methods are wanted to test the validity of the Nernst equation, $Q = RT^2 \epsilon \frac{d \log_{10} K}{dt}$; as regards the latter, no data are available in many cases.

Relationships of a general character are discussed for the hydrochlorides of nitrogen containing bases, and certain sodium salts of phenols and carboxylic acids. The effect on thermoneutrality and basic constants by the introduction of a second amino-grouping is considered, and it is shown that if attached to nitrogen it produces an *increase*, but a *decrease* if attached to carbon, hydrazin being an exception. Similar arguments are adduced as to the effect of the substitution in the benzenoid amines by various elements and groupings, and it is shown generally that the order of strength of such derivatives is $p > m > o$ in the majority of cases. The great increase in thermoneutrality and basic constants (almost complete disappearance of hydrolysis) caused by the addition of hydrogen to pyridine and quinoline appears to point to a total difference of chemical structure.

Finally, it is pointed out that determinations are required of hydrolysis values at considerable dilution of certain metallic chlorides, as determinations are either completely wanting, or, if obtained, are discordant, and a hope is expressed that the record, however imperfectly presented by the author, may lead to a further interest in the subject.

Dr. G. Senter thought there was some doubt as to the connection between hydrolysis and heats of neutralisation—the greater the one the less the other—arrived at in the paper.

Dr. A. C. Cumming asked how the author got over the difficulty of impurities in the water working at such extreme dilutions.

Dr. V. H. Veley agreed that there were factors other than neutralisation involving heat changes. By his method the effect of impurities was eliminated.

A paper by Dr. Joseph Knox, entitled "*A Study of the Sulphur Anion and of Complex Sulphur Anions*," was communicated by Dr. A. C. Cumming.

The solubility of HgS (red and black) in Na_2S, K_2S, and BaS solutions has been determined, and has been found to depend on the formation of the complex anion, HgS_2''. By its greater solubility in these solutions the black modification of HgS has been shown to be the unstable form. The temperature-coefficient of the solubility in Na_2S between 25° and 33° is small and negative. The effect of adding NaOH to the Na_2S is to increase greatly the solubility of HgS, owing to the

diminished hydrolysis of Na_2S. In the presence of a large excess of NaOH the HgS dissolved becomes practically equivalent to the Na_2S, pointing to the formula Na_2HgS_2 for the complex. The formula has been confirmed by E.M.F. measurements, and by an investigation of the complex by the method of Bodländer (*Zeit. Physik. Chem.*, 1902, xxxix., 307). The constant for the formation of the complex anion from the ions Hg'' and S'' is—

$$k = \frac{[HgS_2'']}{[Hg''][S'']^2} = 5{\cdot}1 \times 10^{54}.$$

From a solution saturated with both Na_2S and HgS a crystalline double sulphide of sodium and mercury—$2NaS,5HgS,3H_2O$—has been isolated and analysed.

The solubility of HgS in Na_2S_2 solutions is about half that in the corresponding Na_2S solutions, and the same complex anion HgS_2'' probably predominates here too.

From the study of the complex formation between HgS and Na_2S it is concluded that Na_2S in dilute solution is practically completely hydrolysed into NaOH and NaHS, and this conclusion is confirmed by independent dilatometric experiments on the catalysis of the decomposition of diacetone-alcohol by dilute Na_2S solutions (*cf.* Küster, *Zeit. Anorg. Chem.*, 1905, xliii., 53).

With the aid of the various constants obtained in the investigation, the constitution of the more important sulphide solutions used analytically in sulphide precipitations has been determined, and the approximate concentrations of the S'' and other ions in such solutions are tabulated.

By measuring the E.M.F. of the metals in solutions of Na_2S of known S''-ion concentration, the solubility products of HgS, Ag_2S, CuS, and PbS have been determined: $[Hg''][S''] = 2{\cdot}8 \times 10^{-54}$, $[Ag']^2[S''] = 3{\cdot}9 \times 10^{-50}$, $[Cu''][S''] = 1{\cdot}2 \times 10^{-42}$, $[Pb'']S''] = 2{\cdot}6 \times 10^{-15}$.

Dr. F. Mollwo Perkin referred to the bearing of the paper on analytical problems.

Dr. G. Senter asked whether the author in his experiments had reached equilibrium in both directions.

Dr. A. C. Cumming, in reply, said that Dr. Knox had done so in some cases.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

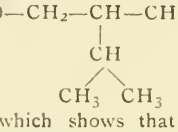
Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 4, January 27, 1908.

Abnormal Mobility of the Ions of the Rare Earths.—Jules Roux.—The mobilities of the ions of the rare earths are much greater than those of monovalent and divalent ions, and also greater than the negative trivalent ions, except in the case of the samarium ion, the mobility of which is of the same order of magnitude as monovalent ions. This indicates that possibly the rare earths can be separated either by diffusion or by electrolysis. The mobility of the lanthanum ion increases from 111 at 18° to 131 at 25°.

Radio-activity of Plombières Waters.—André Brochet.—The author has determined the radio-activity of the Plombières water, and has obtained numbers which are considerably higher than those found by Cheveneau and Laborde. He has also shown that the emanation extracted from the water of the Capucin spring loses half its activity in four days. There appears to be no connection between the radio-activity of waters and their temperature.

Dissociation of Double Chlorides of Dimercuric Ammonium and Ammonium by Water.—H. Gaudechon.—The compounds $NHg_2Cl.NH_4Cl$ and $NHg_2Cl.3NH_4Cl$, in presence of water at the ordinary temperature, behave like true double salts, which confirms Rammelsberg and Pesci's hypothesis relating to their constitution. Thermochemical data, however, show that in the compound $NHg_2Cl.NH_4Cl$ the group NH_4Cl unites to the group NHg_2Cl with more energy than is usual in the case of double salts. Possibly the molecule contains complex radicles. The decomposition of $NHg_2Cl.NH_4Cl$ is limited by a very low concentration of NH_4Cl in the solution. In boiling water the NHg_2 radicle tends to decompose, giving NH_3, $HgCl_2$, and HgO.

Formula of Fenone.—L. Bouveault and M. Levallois.—Fenone, when treated with sodamide, gives an amide, $C_9H_{17}CONH_2$, from which, by the action of NaBr, diapophenyl urea, $CO<\begin{matrix}NH—C_9H_{17}\\NH—C_9H_{17}\end{matrix}$, is obtained. This urea is decomposed by boiling sulphuric acid into the hydrocarbon, $C_9H_{16} + H_2O$, apofenene. Hence, probably the NH_2 group is attached to a tertiary carbon atom. From apofenene the symmetrical acetone acid, $C_9H_{16}O_3$ or—



can be separated, which shows that in all probability Semmler's formula for fenone is correct.

Essence of Magnolia Kobus.—Eug. Charabot and G. Laloue.—This essence is obtained by the distillation of the branches of the Japanese tree. The principal constituent is anethol, and the essence also contains about 15 per cent of citral.

NOTES AND QUERIES.

"*.*" Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Heat of Combustion.—(Reply to G. M.).—The heat of combustion of Al has been determined by Dr. Strauss, Physicist to F. Knapp, Essen (see Minet, "Production of Aluminium and its Industrial Uses," p. 209). His result is given as 7140 cals. per grm., which works out as 386,988 cals. for Al_2+3O. Thomsen gives 380,200 for the same.—H. R. Ellis.

MEETINGS FOR THE WEEK.

Monday, 16th.—Royal Society of Arts, 8. (Cantor Lecture). "Fuel and its Future," by Prof. V. B. Lewes.

Tuesday, 17th.—Royal Institution, 3. "Membranes—Their Structure, Uses, and Products," by Prof. William Stirling, M.A., LL.D., D.Sc., &c.

—— Royal Society of Arts, 8. (Shaw Lectures on Industrial Hygiene). "Child Workers and Wage Earners," by Miss Nettie Adler.

Wednesday, 18th.—Royal Society of Arts, 8. "Impressionist Painting—its Genesis and Development," by Wynford Dewhurst, R.B.A.

—— Microscopical, 8. Presidential Address, "On Seeds, with Special Reference to British Plants," by Lord Avebury. Exhibition of Mounted Specimens of some of the Rarer Species of Fresh-water Polyzoa, by C. F. Rousselet.

Thursday, 19th.—Royal Institution, 3. "Standardisation in various Aspects—(1) Mechanical Engineering," by R. T. Glazebrook, F.R.S., &c.

—— Royal Society of Arts, 8. (Howard Lecture). "The Navigation of the Air," by H. S. Hele-Shaw, F.R.S., &c.

—— Chemical, 8.30. "Constitution of Electro-negative 'Thiocyanates,'" by A. E. Dixon and J. Taylor. "Improved Form of Pycnometer," W. R. Bousfield. "Quantitative Conversion of Aromatic Hydrazines into Diazonium Salts," by F. D. Chattaway. "Action of Heat on α-Hydroxycarboxylic Acids—Part IV., Racemic αα-Dihydroxyadipic Acid and Meso-αα-dihydroxyadipic Acid," by H. R. Le Sueur. "Spontaneous Crystallisation of Sodium Sulphate Solutions," by H. Hartley, B. M. Jones, and G. A. Hutchinson. "Quantitative Relations of Salts of Thallium and its Separation from Silver," by J. F. Spencer and Miss M. Le Pla. "Constitution of Hydroxyazo-compounds—Action of Diazomethane and of Mercuric Acetate," by C. Smith and A. D. Mitchell.

Friday, 20th.—Royal Institution, 9. "Recent Earthquakes," by Prof. John Milne, F.R.S., &c.

Saturday, 21st.—Royal Institution, 3. "Electric Discharges through Gases," by Prof. J. J. Thomson, F.R.S.

THE CHEMICAL NEWS.

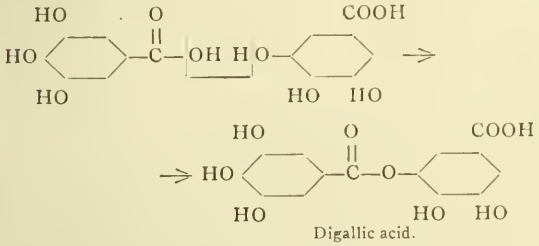
Vol. XCVII., No. 2521.

PRELIMINARY NOTE ON THE CONSTITUTION OF GALLOTANNIC ACID AND OF TANNINS IN GENERAL.

By STEWART J. LLOYD, Chicago University.

For some time the author has been investigating the structure of gallotannic acid and some of its derivatives, and although the experimental work has not yet been carried far enough to justify its publication in detail, the main results are perhaps sufficiently definite to be of service to other workers in the same field.

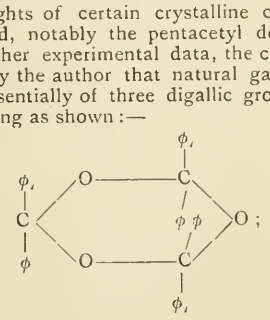
Until the discovery, in 1890, by Llavetsky, that natural gallotannic acid was optically active, it was considered, and quite justly, by chemists to be identical with digallic acid which is prepared by the condensation of two molecules of gallic acid.



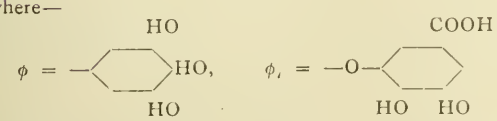
Digallic acid.

As, however, digallic acid contained no asymmetric carbon atom, attention was immediately drawn to the discrepancy, and differences were soon found in the physical, chemical, and physico-chemical properties of the two substances. Owing to the extraordinary difficulty of obtaining gallotannic acid pure, its optical activity was for a time attributed to the presence of a foreign substance, but the careful work of Rosenheim and Schidrowitz proved it to be inherent in the acid itself (*Journ. Chem. Soc.*, 1898, p. 878). The molecular weight, too, of gallotannic acid could not be obtained even approximately, the numbers varying from 400 to 2400.

From careful measurements in various solvents of the molecular weights of certain crystalline compounds of gallotannic acid, notably the pentacetyl derivative, and from various other experimental data, the conclusion has been reached by the author that natural gallotannic acid is composed essentially of three digallic groups united in a six-element ring as shown :—



where—



The analogy with the trithioketones and thioaldehydes described by Baumann and Tromm is quite striking (*Ber.*, xxiv., p. 1419). The optical activity follows, of course, from the formula, and we should expect a structurally inactive *cis*-form as well. There are several tannins from different plants resembling gallotannic acid very closely, so closely indeed that chemical identity has frequently been claimed for them. An investigation of these may result in the discovery of the substance in question.

Whether or not the other group of tannins, of which oak-bark tannin is the best known member, and which reduce to pyrocatechin instead of to pyrogallol, possess an analogous structure, has not yet been learned. The rather difficult investigation of this department of organic chemistry should however be somewhat facilitated by the knowledge of the existence in it of carbon-oxygen rings.

THE FALSIFICATION OF NITRO-COTTON WITH MERCURIC CHLORIDE AND ITS DETECTION.

By JAMES MOIR, D.Sc.

Mercuric chloride is frequently added to wet collodiou cotton, ostensibly to prevent its becoming mouldy, but sometimes also to make it pass the official heat test, even when it is really defective.

Ordinary tests for mercury fail because $HgCl_2$ cannot be extracted (except by volatilisation) owing to its affinity for organic matter. I have therefore invented the two following simple processes :—

(a). *Combination of Hargreaves and Rowe's Method with E. A. Mann's Method.*—The moist cotton, along with a piece of (ignited) silver foil is placed in a flask immersed in boiling water, and air is aspirated through it, and then through potash bulbs containing 2 per cent sulphuric acid. After two hours the $HgCl_2$ which has escaped the silver is deposited thereon by using the foil as anode in electrolysing the dilute sulphuric acid from the bulbs (two hours with about 4 volts required). The foil is dried and sublimed on to a microscope slide, as in the other methods.

(b). *Conversion into Non-volatile Compound.* — The cotton is extracted with hot very weak KI solution, and the extract (containing K_2HgI_4) concentrated to a small bulk and electrolysed. Iodine separates on the platinum basin used as cathode, and the whole of the mercury collects on the gold or silver foil anode after two or three hours, and is worked up as above. The latter method is the quickest and most sensitive I have tried as yet, and has the advantage of having no danger of explosion attached to it.—*Journal of the Chemical, Metallurgical, and Mining Society of South Africa*, viii., No. 7.

PENTAVALENT BISMUTH.

By E. B. HUTCHINS, jun., and VICTOR LENHER.

Peculiar interest has been attached to investigations of a higher state of valence than that of three with bismuth. Its many analogies to the other members of the fifth group of the periodic system have caused the pentavalent condition to be sought for repeatedly. Pentavalent arsenic and pentavalent antimony are well known ; both the oxides and types of the halides exist with these elements. With bismuth as the element having the highest atomic weight in this series, pentavalent derivatives might reasonably be expected.

Since 1818, when Brandes and Bucholz (*Schweigger's J. Chem. Phys.*, xxii., 27) prepared an oxide of bismuth containing more oxygen than the trioxide, many attempts have been made to prepare the pentoxide, a bismuthic acid or a bismuthate. Gutbier (*Zeit. Anorg. Chem.*, xlviii., 162 ; xlviii., 298 ; xlix., 432 ; l. 210) has recently reviewed the various methods which other investigators have used, and with his own work has questioned the acidic character of the higher oxides of bismuth. The authors have repeated most of the methods given for the preparation of these

oxides, and have obtained products by the various reactions whose analyses corresponded to the tetroxide, potassium bismuthate, and impure bismuthic acid. It appears that although none of the higher products of oxidation of bismuth except the tetroxide are stable, yet under the proper conditions, it is possible to have a higher state of oxidation than the valence of three.

Very little attention has, however, been directed to the study of other derivatives than the oxygen type. Muir fused together sulphur and bismuth trichloride and obtained BiSCl but not $BiSCl_3$ (*Journ. Chem Soc.*, xxxix., 22). He also treated Bi_2O_3 with chlorine with the view of obtaining $BiOCl_3$ analogous to $POCl_3$, but obtained only $BiCl_3$. Rauter states that when he treated bismuth pentoxide with silicon tetrachloride he obtained bismuth trichloride as the product (Liebig's *Annalen*, cclxx., 251).

In order to ascertain the action of chlorine on bismuth trichloride at very low temperatures, some of the dry powdered salt and some clear crystals were introduced into a test-tube which was placed in a Dewar bulb containing liquid air. Chlorine gas was passed into the tube, and it at once assumed the solid state. When a large excess of the solid chlorine had collected in the tube, it was withdrawn from the bulb and the solid chlorine allowed to melt. The trichloride was then well shaken with the liquid chlorine and the two returned to the liquid air bulb, where it was kept for an hour. The trichloride remained unchanged in appearance during the entire course of the experiment. After the chlorine had been allowed to spontaneously evaporate, analysis of the powdered material showed it to contain 33·2 per cent of chlorine. From this experiment it is evident that bismuth pentachloride is not formed by the action of solid or liquid chlorine upon the trichloride. Other similar experiments were conducted in which the trichloride was kept in contact with chlorine at $-15°$ for several hours. In no case was the chloride changed in appearance by the action of the chlorine, nor could an excess of chlorine above that required for the trichloride be detected by analysis.

A small quantity of impure bismuth pentoxide was maintained at a temperature of $-10°$ and dilute hydrochloric acid added. The pentoxide dissolved at that temperature with the evolution of chlorine gas. Experiments looking to the formation of double halides of pentavalent bismuth likewise proved fruitless. A hydrochloric acid solution of bismuth trichloride was saturated with chlorine at $-10°$ and solid ammonium chloride added; the solution was then concentrated over sulphuric acid. Colourless crystals separated which on analysis proved to be $BiCl_3,2NH_4Cl$. This salt is described by Deherain (*Comptes Rendus*, liv., 726).

$CsICl_2$, the perhalide of Wells and Penfield (*Am. Journ. Sci.*, xliii., 27), was dissolved in water and a molecular quantity of bismuth trichloride added; chlorine was passed through the hot solution, when a yellow crystalline salt separated at once. Analysis showed this substance to contain 35·05 per cent cæsium, 37·0 per cent of bismuth, and 27·8 per cent of chlorine. The compound is therefore $2BiCl_3,3CsCl$, which has been described by Brigham (*Am. Chem. Journ.*, xiv., 181). In a similar manner bromine was added to a hot solution of cæsium tribromide and bismuth tribromide in hydrobromic acid. In this experiment a finely divided yellow precipitate was obtained which was quite insoluble in hydrobromic acid, but readily soluble in hydrochloric and nitric acids. Analysis showed this to be a new salt corresponding to the formula $2BiBr_3,3CsBr$, as it contained 46·9 per cent bromine, 27·0 per cent cæsium, while the theoretical for $2BiBr_3,3CsBr$ is 46·8 per cent bromine, 27·1 per cent bismuth, and 26·1 per cent cæsium.

It is evident from the preceding work and from the experiments of others that while bismuth can exist in a higher state of valence than three with oxygen, thus far the halogens have not been combined with bismuth in any higher ratio than that of the valence of three.—*Journal of the American Chemical Society*, xxix., No. 1.

A METHOD FOR THE VOLUMETRIC ESTIMATION OF TITANIUM

By H. D. NEWTON.

About forty years ago, F. Pisani (*Comptes Rendus*, lix., 298) stated that titanic acid could be estimated by reduction with zinc in hydrochloric acid solution, the action being hastened by gentle heat, and, after the reduction was complete, pouring off the undissolved zinc, washing, and titrating with potassium permanganate. Pisani, while stating that the above procedure gave excellent results, gave no test analyses. Marignac (*Zeit. Anal. Chem.*, vii., 112) applied Pisani's method, shortly after its publication, to the estimation of titanic acid in the presence of niobic acid. Marignac's procedure differed slightly, however, from Pisani's, in that the titanic acid was reduced out of contact with the air, by means of a long bar of zinc extending well up into the neck of the flask, the zinc being removed after the reduction was completed and the solution titrated directly in the flask. The test analyses given are good, though the results are low, especially when large quantities of titanic acid are used.

Somewhat later, Wells and Mitchell (*Journ. Am. Chem. Soc.*, xvii., 878) modified Pisani's method, as improved by Marignac, by using sulphuric acid solutions and protecting the solution from oxidation during cooling and titration by means of a stream of carbon dioxide. The experimental results are still below the theory, the greater portion of the error being attributed by the authors to the oxidising action of the air, which gained access to the liquid in spite of the precautions taken.

The work to be described is a result of an attempt to eliminate the oxidising action of the air by reducing and cooling under an atmosphere of hydrogen, and converting the equivalent of titanium sesquioxide to ferrous sulphate by introducing an excess of ferric salt. A cold solution of a ferrous salt, as is well known, is very slowly acted upon by atmospheric oxygen (Peters and Moody, *Am. Journ. Sci.*, xii., 367).

The reaction between the salts of titanium and iron takes place according to the following equation:—

$$Ti_2(SO_4)_3 + Fe_2(SO_4)_3 = 2Ti(SO_4)_2 + 2FeSO_4.$$

For this work, the titanium solutions were made by treating re-crystallised potassium titanofluoride with concentrated sulphuric acid, evaporating the mixture to the fuming point of the acid, and diluting to a known volume. The resulting solutions were standardised by the basic acetate method, slightly modified in the present case, owing to the absence of any iron in the solutions used (Gooch, *Am. Chem. Journ.*, vii., 283).

Measured portions of these solutions were drawn into a flask of about 100 cc. capacity, a definite amount of zinc having a known iron content was added, the solution finally made up to such volume as to contain about ten per cent of concentrated sulphuric acid, this strength of acid being sufficient to hold the titanic acid in solution and yet be without oxidising action on the reduced oxide. A rubber cork, through which passed a delivery tube and small separating funnel, was inserted into the mouth of the flask. Gentle heat was applied, while an atmosphere of hydrogen was constantly kept above the liquid until all the zinc was dissolved and the solution cooled, a process which generally took about an hour. An excess of ferric sulphate was passed through the separating funnel and followed at once by cold, freshly distilled water until the flask was filled to the neck. The contents of the flask were then poured into a litre flask containing more cooled distilled water, and the whole immediately titrated with tenth-normal potassium permanganate.

In Table I. are given results obtained by the foregoing procedure. In Table II. are recorded similar experiments in which larger amounts of titanic acid were taken.

These experiments show that it is possible to reduce titanic acid by means of zinc in a small flask and to

determine the titanium with success, by reducing in an atmosphere of hydrogen, adding an excess of ferric sulphate, and titrating the resulting, and equivalent, ferrous salt with potassium permanganate. The factor for metallic iron divided by 0·689 gives the factor for titanium dioxide.

Table I.

Titanium sulphate.	$KMnO_4$.	TiO_2 taken.	TiO_2 found.	Error.
Cc.	Cc.	Grm.	Grm.	Grm.
30	6·50	0·0520	0·0523	+0·0003
30	6·52	0·0520	0·0524	+0·0004
30	6·45	0·0520	0·0519	−0·0001
30	6·50	0·0520	0·0523	+0·0003
30	6·48	0·0520	0·0521	+0·0001
30	6·42	0·0520	0·0518	−0·0002
30	6·50	0·0520	0·0523	+0·0003

Table II.

25	19·95	0·1596	0·1599	+0·0003
25	19·93	0·1596	0·1598	+0·0002
25	19·95	0·1596	0·1599	+0·0003
25	19·90	0·1596	0·1595	−0·0001
25	19·95	0·1596	0·1599	+0·0003
25	19·95	0·1596	0·1599	+0·0003
25	19·90	0·1596	0·1595	−0·0001
25	19·85	0·1596	0·1591	−0·0005
25	19·95	0·1596	0·1599	+0·0003
25	19·88	0·1596	0·1594	−0·0002
25	19·95	0·1596	0·1599	+0·0003
25	19·95	0·1596	0·1599	+0·0003

In conclusion, I wish to thank Prof. F. A. Gooch for advice and assistance given during the progress of this work.—*American Journal of Science*, xxv., p. 130.

THE ATOMIC WEIGHT OF CHLORINE.*

By WILLIAM A. NOYES and H. C. P. WEBER.

The ratio of the atomic weights of oxygen and of chlorine is one of extreme importance, on account of the number of atomic weights based either directly or indirectly upon the atomic weight of chlorine.

During the last few years alone, since the determination of the ratio silver to chlorine by Richards and Wells (*Journ. Am. Chem. Soc.*, xxvii., 459), the atomic weights of a considerable number of the common elements have been determined, basing them on the value of chlorine. These values have been calculated on the oxygen basis, assuming that the ratio silver : oxygen :: 107·93 : 16 is correct. Guye and Ter-Gazarian have called attention to a possible source of error in the chlorate ratio of Stas, correction for which would bring the value of silver down to 107·89 (*Comptes Rendus*, cxliii., 411). The newly accepted value 14·01 for nitrogen also points to the lower value of 107·89. Very nearly at the close of this work conclusive evidence has been presented by Richards and Forbes (*Journ. Am. Chem. Soc.*, xxix., 808) and by Richards and Jones (*Journ. Am. Chem. Soc.*, xxix., 826) that the value 107·93 for silver is too high. The only direct comparison between hydrogen and chlorine which we have is that of Dixon and Edgar (*Phil. Trans.*, ccv., 169, Series A.; Chemical News, xci., 263)—the determinations by Deutsch (Dissertation, 1905) in the laboratory of Professor Guye, were scarcely of sufficient accuracy to be considered as atomic weight determinations. In this determination hydrogen was made to burn in an excess of chlorine. The hydrogen was weighed absorbed in palladium and the chlorine in the liquid form in a glass bulb. The hydrogen and chlorine were caused to unite in a large globe of glass containing a small quantity of water to absorb the hydrochloric acid formed. Corrections were applied for the quantity of chlorine remaining uncombined by titrating the amount of iodine liberated by it from a solution of potassium iodide. A further correction was applied for the amount of chlorine used up in liberating oxygen from water, by determining the amount of oxygen set free.

The fact that there was only one such direct determination of the ratio between chlorine and hydrogen, together with the opportunity afforded of carrying out the determination with hydrogen prepared in the same apparatus used for generating the hydrogen in the recent determination of the ratio of hydrogen to oxygen, made a new determination seem to be worth while.

The method we have used, besides being a direct comparison between hydrogen and chlorine, involves the principle of complete synthesis with the determination of the weights of all the substances reacting and of the reaction products formed. Briefly stated, the method consists in weighing the hydrogen absorbed in palladium, and the chlorine in the form of potassium chlorplatinate. The hydrogen is passed over the heated potassium chlorplatinate, from which it removes chlorine to form hydrochloric acid. The hydrochloric acid formed is condensed in a third section of the apparatus and weighed. We have thus the weight of hydrogen used, the weight of chlorine removed, and the weight of hydrochloric acid formed. In this manner two series of ratios, each independent of the other, are obtained.

Working in this manner and with hydrogen prepared under the same conditions and at the same time as that used in the determination of the ratio hydrogen to oxygen by one of us, we believe that we have very favourable conditions for bridging the gap—

$$Ag \rightarrow \mathbf{Cl} \supset \mathbf{H} \rightarrow O.$$

Purification of Materials and Weighing.

Hydrogen.—The hydrogen used in these experiments was prepared and purified in the same manner as described in a previous paper on the atomic weights of hydrogen (Noyes, *Journ. Am. Chem. Soc.*, xxix., 1720; see also Chemical News, xcvii., p. 56 *et seq.*). The gas was taken from the generating apparatus at intervals covered by the period of the work on hydrogen. Consequently all remarks concerning its character and purity as used in the hydrogen-oxygen ratio apply to these determinations. As in that work so in this, two methods of generating the hydrogen were employed. In the last series of determinations the hydrogen was obtained by the electrolysis of a solution of barium hydroxide.

Platinum.—The platinum used in the preparation of potassium chlorplatinate was originally obtained in the form of platinum sponge. The preliminary purification consisted in dissolving this in aqua regia and evaporating to remove nitric acid. The separation from other platinum metals was carried on according to the method of Schneider and Seubert as described in Graham Otto's "Lehrbuch," 5th Ed., iv., 1153.

The solution of chlorplatinic acid was boiled for half an hour with excess of caustic soda, acidified, and the platinum precipitated as potassium chlorplatinate. The chlorplatinate so obtained was reduced with sodium formate. The platinum black was then heated with dilute hydrochloric acid to remove iron and washed until it commenced to go through as colloidal platinum. It was then re-dissolved and the process repeatedly gone through until the mother-liquors from the chlorplatinate precipitation were practically colourless and free from other platinum metals. As the same platinum was continually used and underwent a large number of successive solutions and reductions during the preliminary work, it seems safe to assume that it was sufficiently pure.

Potassium Chlorplatinate.—During the preliminary work it was soon discovered that the preparation of chlorplatinic acid by the use of aqua regia was unsatisfactory. The removal of nitric acid by the process of repeated evaporation was tedious and at best uncertain. To overcome this difficulty and eliminate nitric acid

* From *The Journal of the American Chemical Society*, xxx., No. 1.

entirely, a process of dissolving the platinum electrolytically in purified hydrochloric acid was devised. This proved quite satisfactory, and will be described in the following paper. After solution of the platinum in hydrochloric acid had been effected, the solution, which contained approximately 120 grms. of platinum and measured 500 cc., was evaporated to about one-half its volume in a glass-stoppered wash-bottle. At the same time a current of chlorine was passed through the boiling solution. The chlorine used for this purpose was prepared by the action of pure potassium permanganate upon chemically pure hydrochloric acid which had been previously boiled with a small quantity of permanganate to insure its freedom from bromine compounds. The solution of chlorplatinic acid thus obtained had a beautiful bright colour matching almost exactly that of a 0·1 per cent solution of methyl orange. It contained about 100 grms. of hydrochloric acid in excess, and after filtration and dilution to one litre was used directly for the precipitation of potassium chlorplatinate. For this purpose a solution of potassium chloride was prepared, using an excess of one-third above the theoretical quantity dissolved in one litre of water. The excess of potassium chloride as well as the excess of hydrochloric acid in the chlorplatinic acid were deemed necessary to check hydrolytic decomposition. For the same reason the precipitation of potassium chlorplatinate was carried out with as concentrated solutions as practicable. The precipitation itself was carried out by pouring the platinum solution into the potassium chloride in a fine stream, the precipitate meanwhile being agitated thoroughly by a current of air. In some cases as much as four hours were spent in precipitating 300 grms. of potassium chlorplatinate. The potassium chlorplatinate so obtained was of a pale yellow colour, resembling precipitated sulphur, and was microcrystalline. It was filtered from the mother-liquor by means of a suction-pump, washed with water, and finally with alcohol and ether. After having been removed from the hardened filter, it was heated for some time in a large platinum dish on an electric air-bath until the greater part of the moisture retained had been driven off. The quantity necessary for one determination was then transferred to a hard glass tube. This tube was placed in a cylindrical air-bath which could be raised to a temperature of 400°. The potassium chlorplatinate was gradually raised to this temperature, a current of air, dried successively by sulphuric acid and phosphorus pentoxide, passing over it continuously. The behaviour of the salt under these conditions served as a criterion of its purity. At the exit of the current of gas, a wash-bottle was placed containing a drop of methyl orange. At first a small quantity of moisture and hydrochloric acid passed off. Finally, however, a point was reached where no further hydrochloric acid could be detected in the issuing gas stream. At this point the heating was stopped, usually after the chlorplatinate had been heated to 400° for about seven hours, or more. It seems that the chlorplatinate, when pure, will stand the temperature of 400° indefinitely in a non-reducing atmosphere, without suffering any change chemically. No appreciable quantity of hydrochloric acid could be detected after the hydrochloric acid and water held mechanically had once been driven off. This all, provided the salt was pure to start with. In the first trials, in which the chlorplatinate had been prepared by the use of aqua regia, its behaviour was entirely different. In these cases decomposition set in in the neighbourhood of 250° and seemed to go on progressively throughout the whole mass of the salt.

After having been dried in this manner, the chlorplatinate was transferred to the final apparatus with little or no exposure to the air, through an opening which was sealed off after filling. In this it was subjected to final drying at 350° and evacuation, as described under the manipulations.

Potassium Chloride.—As a starting point for the preparation of pure potassium chloride, the purest commercial article obtainable was taken. This was first re-crystallised from a solution made slightly alkaline with potassium hydroxide to remove traces of ammonia which were present. The salt was then re-dissolved in water and chlorine passed through the hot solution for several hours, after which it was concentrated and the potassium chloride allowed to crystallise out. Following this the salt was re-crystallised five times from water, precipitated three times by alcohol, and finally precipitated from aqueous solution by purified hydrochloric acid gas. The crystals in these varied processes were separated from the mother-liquors by centrifugal drainage.

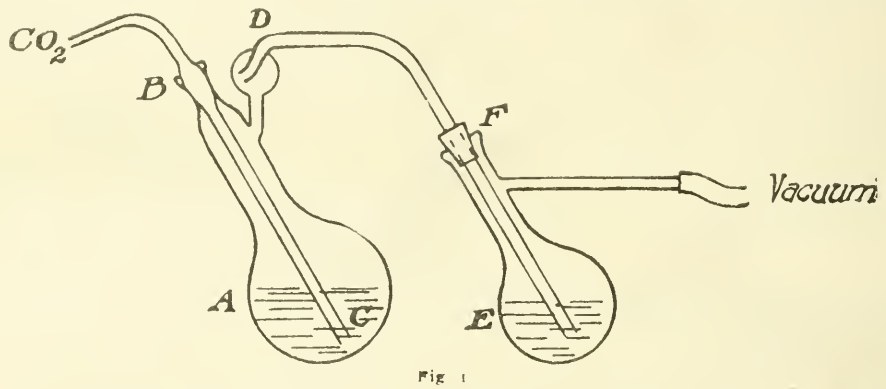


Fig. 1

This potassium chloride certainly contained less bromine than 1 in 50,000. To test for bromine the following process, a modification of that described by Andrews, was adopted (*Journ. Am. Chem. Soc.*, xxix., 275).

The flask A is fitted with a ground glass joint at B which ends in an extremely fine capillary at C. The side tube D has a trap to prevent spray from being carried over. An ordinary distilling flask is affixed to the end of this side tube with a rubber stopper in such a manner as to bring the side tube well into the bulb of the flask E. The flask A is charged with 200 cc. of distilled water, 20 cc. of N/5 potassium iodate, and 20 cc. of 2 N nitric acid. The flask E contains about 5 cc. of a 4 per cent solution of potassium iodide (which must not liberate iodine upon being acidified). The flasks are then connected by means of the stopper at F and vacuum applied. The capillary tube which is ground into the flask at B is connected with a carbon dioxide generator, and after vacuum has been applied, should yield a fairly steady stream of bubbles through the liquid, so as to insure regular boiling and at the same time not appreciably to diminish the vacuum. It is desirable to have a pure neutral gas such as carbon dioxide or nitrogen passing through the capillary, since traces of reducing substances in the air used would vitiate the results. The gas passing through the capillary, besides insuring regular boiling, acts as a diluent for the

steam formed and as such checks the reaction $H_2O + Br_2 = 2HBr + O$.

The flask containing the potassium iodate and nitric acid mixture is then heated on the water bath until 100 cc. have distilled into the flask containing the potassium iodide. If the resulting distillate is coloured by the presence of free iodine, the process is repeated after adding water to make up for the quantity distilled off, until a satisfactory blank is obtained. Then 3—5 grms. of the potassium chloride to be tested are dissolved in a little water and added to the flask containing the iodate and the volume of the solution made up to 250 cc. again. The distillate containing the free iodine corresponding to the amount of bromine distilled over, is then titrated with a solution of thiosulphate corresponding to 1 mgrm. of bromine per cubic centimetre. To 5 grms. of potassium chloride which had been treated until blank distillates were obtained the following quantities of bromine were added and found :—

Added ..	1	0·5	0·3	0·1 mgrm.
Found ..	1	0·52	0·36	0·12 mgrm.

The potassium chloride used for precipitating potassium chlorplatinate contained less than 0·1 mgrm. bromine in 5 grms. or 1 : 50,000. This amount, it is safe to assume, was further reduced in the preparation of potassium chlorplatinate.

Hydrochloric Acid.—The hydrochloric acid used in the preparation of pure hydrochloric acid was free from sulphuric and nitric acid. It was treated by allowing chlorine to bubble through it for one day. Following this, air was bubbled through the acid saturated with chlorine until the chlorine was expelled and the acid was again colourless. Usually the air was left passing through the acid over night, a reduction of about one-fifth in the volume of the acid, due to evaporation, taking place with the removal of the excess of chlorine. During the manipulations in preparing chlorplatinic acid, it was further subjected to the action of chlorine twice, namely, during electrolysis of the platinum and on evaporation of the platinum solution.

Chlorine.—All the chlorine used was generated by the action of pure potassium permanganate on hydrochloric acid which had been previously boiled with a small quantity of potassium permanganate.

Water.—The water used was obtained by re-distilling distilled water with alkaline permanganate, rejecting the first part of the distillate until it no longer contained ammonia.

Balance and Weights.—The balance and weights were identical with those described under the atomic weight of hydrogen (Noyes, *Journ. Am. Chem. Soc.*, xxix., 1723). The air of the balance case was dried by means of a current of air as described in the previous paper. Each piece of apparatus was weighed with a corresponding counterpoise approaching it within 1 cc. in volume and 30 grms. in weight. In the case of the hydrogen the counterpoise was within 0·3 cc. of the volume and 2 grms. of the weight of the palladium tube.

All pieces were rinsed with distilled water after having been used in a determination. Having been wiped dry, they were suspended for some time in a desiccator through which a current of dry air was passing, before being transferred to the dry air of the balance. For the hydrogen apparatus twelve to twenty-four hours were allowed in order to attain constant surface conditions. The current of air through the balance was stopped fifteen to twenty minutes before a weighing was made. Duplicate weights were taken at intervals of an hour or more and rarely differed by more than 0·05 mgrm.

Weights.—The weights were calibrated to vacuum standard here in the Bureau of Standards. The small correction necessary on account of the difference in volume between the brass and platinum weights was included in a table with the corrections for the errors of the weights.

(To be continued).

THE USE OF TIN AS A CATHODE FOR THE RAPID QUANTITATIVE ELECTROLYTIC DEPOSITION OF ZINC, COPPER, SILVER, CADMIUM, AND NICKEL.*

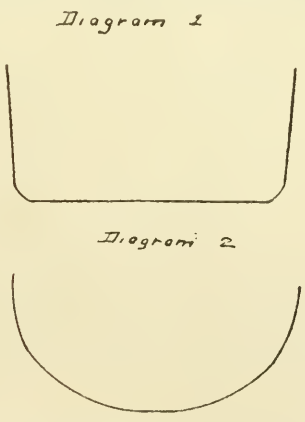
By LAURENCE T. SHERWOOD and GELLERT ALLEMAN.

The high price of platinum, together with other minor considerations, led to an investigation in the Laboratory of the Department of Chemistry, Swarthmore College, in order to determine if metallic cathodes, other than platinum, could be used for the quantitative electrolytic deposition of various metals, and, if so, to determine the exact conditions productive of the best results. While it is intended to continue this investigation, using other metallic cathodes, especially tungsten, this article has to deal entirely with the tin cathode, and the deposition on it of the five elements named in the title.

Attention is directed to the fact that all the results obtained are published in the tables—none having been rejected.

While not so generally applicable as platinum, it was found that for the estimation of the metals enumerated, tin could be substituted for the more expensive material. The attempt has not yet been made to use this cathode in determining any other of the metals, but judging from the work thus far it seems quite possible that it may be used for all of those which are deposited in the metallic state.

Platinum has been regarded as about the only suitable cathode material because of its insolubility and immunity from corrosion, and, of course, these were anticipated as the chief defects of tin. The solvent action of electrolytes was especially feared, but with certain precautions, which



will be mentioned under the special considerations, there was no loss of tin during the determination even with such powerful solvents as sulphuric acid and potassium cyanide. Corrosion of other natures gave no trouble whatever.

The following general facts regarding the care of the dishes may be worth mentioning :—

Solutions which have not a solvent action may, during the progress of an analysis, be heated in them upon a sheet of asbestos (thickness exceeding a quarter inch) or upon an electric stove without fear of oxidising the tin.

On account of the low melting-point of tin the dish cannot, of course, be held in the free flame nor set upon hot asbestos or an electric stove, if empty.

The surface should be kept bright by an occasional scouring with fairly coarse sea-sand.

For reasons which will appear later it is preferable, but not necessary, to keep separate dishes for depositions of each particular metal.

The first dishes were made of Kahlbaum's tin, cast in an

* From the *Journal of the American Chemical Society*, xxix., No. 7.

TABLE I.

$ZnSO_4.7H_2O$ = Zn, in grm.	NaOH, in grms.	Volume in cc. when diluted.	Approximate temperature at start.	Current N.D.$_{100}$ = A.	Volts.	Time, in minutes.	Zn deposited, in grms.	Error in per cent of Zn in $ZnSO_4.7H_2O$.
0·2496	8	100	65°	5	5	30	0·2490	0·05
						30	0·2495	0·01
						30	0·2501	0·05
						25	0·2502	0·06

TABLE II.

						30	0·2494	0·02
						30	0·2501	0·05
						30	0·2492	0·03
						30	0·2494	0·02
0·2496	8	100	65°	3	7	30	0·2494	0·02
						25	0·2582	0·13
						25	0·2536	0·37
						25	0·2515	0·18
						25	0·2507	0·10
						25	0·2505	0·08
						25	0·2508	0·07
						25	0·2498	0·02
						25	0·2517	0·16
						25	0·2495	0·04
0·2500	8	100	65°	3	7	25	0·2502	0·02
						25	0·2417	0·75
						25	0·2448	0·47
						25	0·2476	0·22
						25	0·2486	0·13

TABLE III.

$ZnSO_4.7H_2O$ = Zn, in grm.	$CH_3.COONa$, in grms.	30 per cent acetic acid, in cc.	Volume in cc. when diluted.	Approximate temperature at start.	Current, N.D.$_{100}$ = A.	Volts.	Time, in minutes.	Zn deposited, in grm.	Error in per cent of Zn in $ZnSO_4.7H_2O$.
								0·2509	0·08
								0·2496	0·03
0·2500	3	0·2	100	20°	3	18·5—11·5	15	0·2499	0·01
								0·2489	0·10
								0·2491	0·08

TABLE IV.

								0·2494	0·05
								0·2483	0·15
								0·2505	0·05
								0·2491	0·08
								0·2504	0·04
								0·2474	0·23
								0·2488	0·11
								0·2509	0·08
0·2500	3	0·2	100	20°	2	12·5—9·5	15	0·2484	0·14
								0·2483	0·15
								0·2497	0·03
								0·2513	0·12
								0·2490	0·09
								0·2489	0·10
								0·2517	0·16
								0·2496	0·03
								0·2516	0·15
								0·2480	0·18

NOTE.—Speed of rotator was 700 revolutions per minute.

TABLE V.

$ZnSO_4.7H_2O$ = Zn, in grm.	$CH_3.COONa$, in grms.	30 per cent acetic acid, in cc.	Volume in cc. when diluted.	Approximate temperature at start.	Current N.D.$_{100}$ = A.	Volts.	Time, in minutes.	Zn deposited, in grm.	Error in per cent of Zn in $ZnSO_4.7H_2O$.
0·2500	3	0·2	100	20°	2	18—13	17	0·2500	0·00
							17	0·2493	0·06
							17	0·2500	0·00
							17	0·2497	0·02
0·2500	3	0·2	100	65°	2	14—11	16	0·2496	0·03
							16	0·2490	0·09
							18	0·2498	0·02
							16	0·2496	0·03
							17	0·2495	0·04

iron mould of the shape represented by cross-section diagram No. 1, and cut down on a lathe to a suitable weight (70 to 80 grms.). The dimensions were :—Diameter of top, 8 cm. ; diameter of bottom, 7 cm. ; height, about 3·3 cm. The total inside surface was approximately 115 sq. cm., which was equivalent to about 100 sq. cm. when 100 cc. of liquid was rotating inside. Most of the work on zinc was done with these dishes, but they were unsatisfactory both in their form and on account of pores in their surfaces due to imperfections in the castings. The dish which has thus far given the best results has a form indicated by cross-section diagram No. 2.

These were spun by J. Bishop and Son, from sheet block tin (No. 18 B. and S. gauge) bought of Messrs. Eimer and Amend. The diameter of the top was 9 cm. ; the total surface about 125 sq. cm., which was equivalent to about 100 sq. cm. when 100 cc. of liquid was rotating within. They weighed about 65 grms. Owing to the softness of tin, the edge of the dish where it is grasped by the forceps in weighing should be as thick as consistency will permit.

To economise time the rotating anode was used in practically all the investigations. The forms used consisted of platinum wire respectively 1·4 mm. and 1·1 mm. in diameter (Nos. 17 and 19, B. and S. gauge), bent into spirals. The former size was slightly preferable. The spirals were depressed in the centre, conforming somewhat to the shape of the dish. Their diameter was 3·5 cm. The anodes were inserted in the motor shaft. The motors supplied by the Electro-Dental Manufacturing Co., of Philadelphia, were wound to run on a 110 volt lighting circuit, and had a speed of 500 to 700 revolutions per minute. While they answered practically all purposes it is recommended if this form of rotator is used that the maximum speed be at least 1000 revolutions per minute. A lamp resistance could be put in the circuit to diminish this speed to any desired. Within the range of speeds used there was hardly a perceptible difference in the character of the metallic deposits.

Zinc.—Methods outlined by Exner were adapted for this metal, first using a platinum dish, and later tin (*Journ. Am. Chem. Soc.*, xxv., 900). With a few exceptions, probably due to some slightly different conditions, his methods served very well. A few experiments showed also that Classen's method, using ammonium oxalate and tartaric acid as electrolytes (*Ber.*, xii., 1622), could probably be used with the tin cathode. However, not enough tests were made to decide conclusively.

Table I. records a series of determinations with a platinum dish. The results in Table II. were obtained by almost the same method on the tin cathodes described in diagram No. 1. Sodium hydroxide dissolves tin slowly when no current is passing through it, and the following procedure is therefore recommended. Prepare the sodium zincate by adding the specified amount of sodium hydroxide (in solid form) to the zinc sulphate solution in a beaker. (It is perhaps worth mentioning that Jena glass should be used in preparing the zincate solution, since the strong alkali is apt to dissolve material from the ordinary glass beaker).* Place the dish on its support, and add 30 or 40 cc. of hot water ; *close the circuit*, having the rhesostat adjusted so that about 1 ampère will flow as soon as the electrolytes are added ; introduce the hot zincate solution, dilute to a suitable volume, adjust the electrodes, start the rotator, and allow the full current to pass in. If this procedure is followed, tin will not be dissolved. With the sodium acetate method it is unnecessary to observe the precaution of having the circuit closed before the electrolyte is added.

The deposits on tin exactly resembled those on platinum. They were crystalline, but could easily be washed in the usual manner, and weighed. After weighing, the loose material was wiped and brushed out, and another determination made by depositing on the remaining coating. Moreover, when once coated with zinc, no precautions were necessary to protect the tin from the solvent action of the sodium hydroxide. The adherent coating was very thin, and several depositions could be made before cleaning all the zinc off. To remove the adherent zinc, use dilute hydrochloric or sulphuric acid, or nitric acid with a specific gravity, 1·52. Nitric acid more dilute than this attacked the tin rapidly. After cleaning, the tin surface usually had to be scoured bright with sea-sand. Of course the dishes lost a little weight in cleaning, but with reasonable care they last indefinitely. Dishes in constant use for a year lost less than 2 grms.

In all the determinations of Table II. only two dishes were used, and neither of them was cleaned of the adherent zinc after the series was begun. It is quite possible that by depositing upon the porous zinc surface which was formed after the first few determinations a source of error was introduced, which may account for the inconsistent results in the latter part of the series and throughout Table IV. This point was not thoroughly investigated, but the better results in the first determinations seemed to indicate that that was the case. The irregular results in both Tables II. and IV. are also probably due to the pores and imperfections in the dishes used. Series V. was run on the better form of dish described by diagram No. 2, and the results are consistent. Four or five determinations were made without cleaning off the adherent zinc. It is not advisable to run more than this number in succession.

The time set down by Exner for these depositions was ten to fifteen minutes (see also paper by Ingham, *Journ. Am. Chem. Soc.*, xxvi., 1272). Failure to comply with some conditions made it necessary to take a longer time with the sodium hydroxide electrolyte. The bulk of the metal came down in the first few minutes, but traces remained until the time stated had expired. The time required on tin was the same as that on platinum. As rapidity was not a special object in this investigation no great effort was made to reduce the time, although it should not be difficult to do so. Five ampères, the current used on platinum, gave too loose a deposit on the tin, but no longer time was required with 3 ampères.

Tables III. and IV. record series on platinum and tin respectively with the sodium acetate electrolyte. This method was adapted with practically no change from Exner's conditions. The deposits in both cases were crystalline, and rather loose, but there was no difficulty in washing and weighing them.

The series recorded in Table V. was run by Mr. R. L. Hill, of this laboratory. He used the tin dishes represented in diagram No. 2, and was careful not to run more than four or five determinations on a particular dish without cleaning off the adherent coating of zinc. He also used a slower rotator (550 R. P. M. instead of 700 R. P. M) and a slightly smaller anode, which may account for the extra time required.

(To be continued).

* It must be remembered that Jena glass contains zinc, however, and is somewhat attacked by alkaline solutions. Porcelain would probably be safer.—Ed. *Journ. Am Chem Soc.*

A Remarkable Colour Photograph.—At the present time, when colour photography is in the air and new methods are being exploited on every side, it is interesting to see a good reproduction of a really fine example of general colour photography from nature by the three colour process. The *Photographic News*, one of the most enterprising of publications devoted to the needs of the amateur photographer, is usually well to the front in all up-to-date matters concerning the art of the camera, and is now the first photographic weekly in the world to publish a *fac simile* reproduction in natural colours from nature. This is given in a recent issue of the *Photographic News* as a special mounted supplement, and is a splendid example of colour photography by Mr. H. J. Comley, of Stroud. The picture is a fine example of a perfect rendering of a still-life study of fruit and glass. The wonderful texture and colour of a group of oranges, the transparency of the glass, and the tones of a basket and some crumpled paper are portrayed with a realism that is almost startling.

REVISIONS OF THE THEORY OF ELECTROLYSIS.*

By HENRY S. CARHART, LL.D.

No subject in the whole domain of theoretical electricity possesses more interest to the electro-chemist than the theory of the decomposition of aqueous solutions of salts and acids through the agency of an electric current. For more than a hundred years scientific attention has been converged on it, for it has presented problems both of unusual interest and of unusual difficulty. Its development has not been one of uninterrupted progress, but rather one of leaps and bounds, alternating with seasons of suspended animation. Even with the noteworthy additions of the past twenty years, it cannot be said that all difficulties have yet been resolved. We are in little danger of so completely clearing up the entire field that nothing shall be left for posterity.

An historical review of this subject, biassed it may be by perspective and distorted by the disproportionately large visual angle under which we view recent events, may yet give us more respect for the achievements of the past and less unreserved satisfaction with the advances of our own times.

The earliest record of observed electrolysis dates back of the invention of Volta's dry pile and "crown of cups." The decomposition of water by electrical means was described by Van Troostwijk and Deimann in 1789. It was accomplished by sending a series of electric discharges through water in a narrow glass tube between gold wires whose ends were an inch and a-half apart. The tube was placed vertically, and when the end of the upper wire became uncovered the spark caused the explosive reunion of the mixed gases. These experimenters concluded, contrary to the opinion of many of their scientific contemporaries, that both the hydrogen and the oxygen were obtained from the decomposition of water, and that water consisted of a union of these two gases only. They cited both the synthesis and the analysis taking place in their experimental tube as proofs of their view. But the question as to the manner in which electricity acts to effect the decomposition remained unanswered. They did not obtain the two gases separately, but mixed in the glass tube. An enormous number of discharges were said to be necessary to produce an appreciable volume of mixed gases —14,600 for one-third of a cubic inch.

A little later, Ritter found that 50 or 60 discharges from a Leyden jar through a solution of silver nitrate between silver wires gave a visible deposit of metallic silver on the negative electrode. By reversing the poles this deposit disappeared, and at the same time a new deposit formed on the other wire.

It is therefore obvious that the scientific world was prepared to accept electrolytic decomposition when Volta disclosed his invention of the dry pile and the voltaic battery, or "crown of cups." This disclosure was made in a letter to Sir Joseph Banks, President of the Royal Society of London, dated March 20th, 1800. Before this letter was published in the *Philosophical Transactions* its contents had become known to London physicists, and Nicholson and Carlisle had decomposed water by means of Volta's pile. Carlisle made the acute observation that when a drop of water was placed on the upper plate of the pile to improve the contact between it and the wire of the external circuit, gas was given off; and Nicholson recognised the presence of hydrogen when the wire used was steel. These and similar facts induced them to send the electric current from a pile of thirty-six pairs through river water between brass wires in a glass tube half an inch in diameter. A fine stream of gas bubbles was at once given off from the negative electrode. One-fifteenth of a cubic inch was obtained in an hour and a-half, and when this was mixed with an equal volume of air the mixture exploded on the approach of a lighted wax taper.

Although these observers expected the decomposition of water, they were not prepared for the astonishing fact that, while the hydrogen appeared at the exposed end of one of the wires, the oxygen appeared only at the end of the other, nearly 2 inches distant. This phenomenon was to its discoverers inexplicable. They made the very relevant and acute remark that this new phenomenon "appears to show perhaps a general law of the action of electricity in chemical processes." The explanation of this remarkable fact has ever since engaged the attention and best endeavours of science.

It is worthy of attention also that Nicholson and Carlisle observed that chemical action takes place in a voltaic cell when it functions as a source of current. In other words, they recognised that a voltaic cell is also an electrolytic cell. This is the first of many facts which tell against Volta's contact theory of the electro-motive force of a voltaic cell. Volta himself asserted that the chemical actions going on in a voltaic cell have practically no essential significance.

In this same celebrated year of 1800 Cruikshank decomposed lead acetate between silver wires. A minute or two after connection was made he observed lustrous metallic lead crystals on the negative electrode, while gas was released at the positive. Cruikshank called attention to the fact that only liquids containing oxygen conduct electricity, and he appears to have concluded that electricity seizes on the oxygen and transports it invisibly to the positive pole. Not so far removed from this conception is the present view that the oxygen conveys an electric charge rather than that the charge conveys the oxygen.

The separate appearance of the two products of decomposition at the electrodes was the most noteworthy, and at the same time the most inexplicable fact of electrolysis to all the chemists and physicists of the day. An unknown correspondent in *Nicholson's Journal* expressed himself as follows :—

"I should like to inquire how it can happen in any system that the two components of water can be caused to appear at such a distance from each other. Does the hydrogen from the dissociated particles of water at the zinc side of the pile fly from it at the instant when the oxygen is liberated there? If that is so, why does not one see the gas bubbles on the way? Or does the oxygen migrate from the silver side to the zinc side? Or are there two streams at once?"

It should be remembered that Volta attached an extra zinc plate to the silver at the positive end and an extra silver plate to the zinc at the negative end, both in the case of his dry pile and crown of cups or voltaic battery. Hence, in the early literature the zinc side means the positive and the silver the negative.

Sir Humphry Davy was early in the field of electric research, and at once distanced all his English *confrères* by the number and importance of his detail discoveries. In particular at the outset he obtained oxygen and hydrogen in different tubes separated in the circuit by the interposition of his own person as a conductor, and he proved conclusively that the two gases are evolved in the same relative proportion in which they exist as elements in water. But Sir Humphry Davy added little to the theory of electric action in electrolysis. Near the close of one of his papers published in December, 1800, he remarks :—

"On these facts I shall not presume to speculate. . . . Many observations must be collected, probably, before we shall be able to ascertain whether water is decomposed in galvanic processes. Supposing its decomposition, we must assume that at least one of its elements is capable of rapidly passing in an invisible form through metallic substances, or through water and many connected organic bodies, and such an assumption is incommensurable with all known facts. But a short period has elapsed since philosophers beheld with wonder solid and fluid substances

* Presidential Address delivered at the Seventh General Meeting of the American Electro-chemical Society. From the *Smithsonian Report* for 1906, p. 147.

assuming new modes of existence in different gases. Do not the new phenomena of galvanism authorise us to hope that at no very distant time they will behold even those gases undergoing novel changes, and existing in new and now unknown forms?"

The diffuseness and lack of concreteness of ideas in those early days of the science, before the time of Ohm's law, are strikingly illustrated in the following extract from a syllabus of a course of lectures delivered by Davy in the theatre of the Royal Institution in January, 1802:—

"The agency of the galvanic influence which occasions chemical changes in water, and communicates shocks to the living body, is probably in some measure distinct from that agency which produces sparks and the combustion of bodies. The one appears, all other circumstances being similar, to have little relation to surface in compound circles, but to be great in some unknown proportion as the series are numerous. The intensity of the other seems to be as much connected with the extension of the surface of the series as with their number."

Davy was not at that time able to distinguish between electro-motive force or electric pressure and strength of current.

The long contest waged between the supporters of the contact theory of electric action in a voltaic couple and the chemieal theory is briefly alluded to in this same syllabus, without any clear intimation of the position taken by Sir Humphry himself:—

"M. Volta has supposed that an electric current is always produced by the mere contact of certain different conductors of electricity. But many of the British philosophers have denied this position, accounting for galvanism from the destruction of the equilibrium of electricity in galvanic circles in consequence of the chemical agencies of the different bodies composing them."

On November 20, 1806, Davy read before the Royal Society a Bakerian lecture on "Some Chemical Agencies of Electricity." In this lecture he takes a decided position against the chemical theory of electrical excitation held by many British philosophers. He says:—

"The general ideas advanced in the preceding pages are evidently directly in contradiction to the opinion advanced by Fabroni, and which, in the early stages of investigation, appeared extremely probable, namely, that chemical changes are the *primary* causes of the phenomena of galvanism.

"Before the experiments of M. Volta on the electricity excited by the mere contact of metals were published, I had to a certain extent adopted this opinion; but the new facts immediately proved that another power must necessarily be concerned."

In this same lecture we find suggestions by this distinguished philosopher harmonising with the celebrated theory of Grotthus; but no credit is due to Davy for these suggestions, because Grotthus published his theory in the year 1805 in Rome under the title, "Memoire sur la decomposition de l'eau, et des corps qu'elle tient en Dissolution a l'aide de l'Électricité Galvanique." A second edition followed the next year, and the memoir was also published in the *Annales de Chimie* in 1806. Sir Humphry says:—

"It is very natural to suppose that the repellant and attractive energies are communicated from one *particle to another particle* of the same kind, so as to establish a conducting chain in the fluid; and that this is really the case seems to be shown by many facts. . . .

"In the case of the separation of the constituents of water, and of solutions of neutral salts forming the whole of the chain, there may possibly be a succession of decompositions and recompositions throughout the fluid."

Ostwald says ("Elektrochemie," p. 307) that the different theories proposed to explain the separate evolution of the products of electrical decomposition vied with one another in improbability, and no one of them was free from the most serious objections. When at length one view met with general acceptance it was not so much because of its unconditional excellence as because it was at least relatively the best of all.

Here the account of Grotthus himself relating to the origin of his theory. He says:—

"Volta's pile, which made the genius of its inventor immortal, is an electrical magnet, of which each element—that is, each pair of plates—has both a positive and a negative pole. The consideration of this polarity has suggested to me the idea that a similar polarity might form between the molecules of water when it is acted on by this same electrical agent; and I must confess that this was for me a gleam of light."

Freiherr von Grotthus was a most interesting character. At the age of a year and a-half the death of his father left him to the care of his mother, and he lived with her on her landed estate in Lithuania, near the borders of the Baltic province of Kurland, till his seventeenth year. The taste for science developed in him at an early age, but it was stifled in the most brutal and unsympathetic manner by his teacher, who had neither the taste nor the intelligence for the studies to which the genius of Grotthus inclined. In the year 1803, at the age of eighteen, he went to Leipzig to study, and after six months there he betook himself to Paris, where he listened to the lectures of the most distinguished philosophers of the time. The threatened war between France and Russia compelled him to leave Paris, and he hastened to Naples, where he remained till the end of the year 1805. Through his fortunate acquaintance there with a distinguished English physician named Thomson, who was the owner of a small galvanic apparatus, our young natural philosopher was enabled to repeat the experiments of Professor Pacchiani, which were then exciting much attention. The result was his theory of electrolysis, first published in 1805, when its author was not more than twenty years of age, a theory which held sway for nearly three-quarters of a century, and which has for ever linked his name with the history of electrochemistry.

Under more favourable conditions of birth, education, and surroundings Grotthus might have become one of the most distinguished investigators of his time. But in the autumn of 1807 he felt compelled to return to his ancestral estate, and to busy himself with the duties of manager. Here in the country, in a remote angle of Lithuania, for the most part without literary associates, and lacking often the most essential means of research, he wrung from nature some of her well-concealed secrets and wrote nearly all his contributions to science.

For years he suffered unspeakably from an incurable organic malady. The trouble increased from day to day, and finally reached such an acute stage that he was brought to the rash decision to sever voluntarily the thread of life. He died in 1822 at the age of thirty-seven.

The Grotthus theory of the mechanism of electrolysis does not respond, as we now know, to the facts of later discovery. But since for the first time it made comprehensible the physical possibility of the phenomena of electrolytic decomposition it has enduring value.

Grotthus conceived that a species of polarisation is set up in the water by electrical agency, so that the positively charged elements are turned toward the negative electrode and the negatively charged ones in the other direction. Also, that at the moment of separation of the oxygen and hydrogen from each other a division of their natural charge of electricity takes place, in some way not explained. Attractions and repulsions follow; also the continuous movement of two streams of charged particles in opposite directions, through the process of molecular interchanges, or the exchange of partners whose conjugal bond is chemical affinity. Grotthus does not appear to have got the conception that a current in an electrolyte is the convection of positive and negative charges in opposite

directions, but his theory was directed toward the explanation of the most obvious and novel fact, that the products of the decomposition appear at widely distant points. He distinctly remarks that the process, as he conceives it, involves decomposition at the electrodes only, where the current passes between the electrode and the electrolyte. He says :—

"I conclude, therefore, that if it were possible to produce in water a current of galvanic electricity so that it should describe in it a complete circuit, all the molecules of the liquid which are in this circuit would at the same instant be decomposed and again reformed; whence it follows that the water, although it underlies the action of galvanism, would still always remain water."

Grotthus had no consistent idea of the relation between the charges carried by the components of a molecule and the passage of a current. The current appeared to him only to align the molecular components, and the resulting molecular cleavages and re-formations were due to the attraction and repulsion between the electric charges or their polarity. His conception was crude and imperfect compared with the corresponding concepts of the present time. But it showed at least that the phenomena of electrolysis take place by a conceivable process. If it did not satisfy all intellectual demands, it quieted clamor and bridged the gulf between the known and the inexplicable. It was indeed a gleam of light that has never been effaced, and we owe an everlasting debt of gratitude to the farmer philosopher of Lithuania.

Grotthus gave a vivid picture of the chief phenomenon of electrolysis, the appearance of the separated constituents at the electrodes only. The knowledge of his time scarcely reached beyond this one fact. It was not long, however, before new observations were made which could with difficulty be fitted into his picture.

The essential fact which the theory of Grotthus was incompetent to answer satisfactorily was that the smallest electro-motive force may produce a current through an electrolyte, and the strength of this current follows Ohm's law.

Grotthus assumes that the application of an electromotive force to the electrodes gives rise to a polarised condition of the molecules, and that at the instant of the separation of the hydrogen and oxygen, for example, a separation of their natural charge of electricity takes place, either through contact or friction; so that one part becomes electro-positive and the other electro-negative. This perhaps means that the normal condition of an electrolyte is one of equilibrium with rigidly combined molecules. Grotthus did not appear to conceive of the cleavage of a polarised molecule until current passed.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 5, February 3, 1908.

Heat of Formation of Anhydrous Oxides of Lithium, Calcium, Strontium, and Barium.—M. de Forcrand.—The following are the results the author has obtained for the heat of formation of the oxides of calcium, lithium, strontium, and barium : — *Monoxides.* — $Ca + O = CaO$, + 151·90 cals. ; $Li_2 + O \quad Li_2O$, + 143·32 cals. ; $Sr + O = SrO$, + 137·60 cals. ; $Ba + O \quad BaO$, + 125·86 cals. *Dioxides.*— $Ca + O_2 \quad CaO_2$, + 157·33 cals. ; $Li_2 + O_2 = Li_2O_2$, + 152·65 cals. ; $Sr + O_2 = SrO_2$, + 152·10 cals. ; $Ba + O_2 = BaO_2$, + 145·71 cals. The great resemblance in the numbers found for strontium and lithium, especially in the case of the dioxides, is very striking.

Complex Salts of Iron in which the Iron is Masked.—P. Pascal.—When freshly precipitated ferric pyrophosphate is added to a solution of sodium pyrophosphate, the solubility of the ferric salt is independent of the temperature and of the concentration of the sodium salt. When the solution is saturated the constituents are present in the proportion $(P_2O_7)_3Fe_4 : 3P_2O_7Na_4$. The iron in this solution does not give the ordinary iron reactions except as regards reducing agents, *e.g.*, oxalic acid, ammonium hydrosulphide. Thus, a new complex, to which the author has given the name ferripyrophosphate appears to be present. The sodium salt has the formula $Fe_2(P_2O_7)_3Na_6.9H_2O$. A ferropyrophosphate, $Fe_2(P_2O_7)_3Na_8$, can be prepared by using metaphosphoric instead of pyrophosphoric acid.

New Derivatives of Camphenylone.—L. Bouveault and G. Blanc.—Sodamide gives with camphenylone a compound which is decomposed by water into soda and $C_9H_{14}O + NH_3$, dihydrocampholene amide. This amide, when treated with bromine in presence of sodium methyl alcoholate and methyl alcohol, is transformed into urethane,—

$$C_8H_{15}—CO—NH_2 + Br_2 + 2CH_3ONa = \\ = C_8H_{15}—NH—COOCH_3 + CH_4O + 2NaBr.$$

From the urethane an amine, $C_8H_5NH_2$, apocamphenylamine, can be isolated. Its chlorhydrate gives apocamphenylol with sodium nitrite,—

$$C_8H_{15}NH_2.HCl + NO_2Na = NaCl + N_2 + C_8H_{15}OH + H_2O.$$

By the oxidation of this new alcohol β-isopropylcyclopentanone is formed. Therefore apocamphenylamine is β-isopropylcyclopentylamine, and Wagner's formula for camphenylone is probably correct.

Order of the Addition of Ammonia to the Organic α-Oxides of Asymmetric Structure.—K. Krassousky.—Taking the oxides of propylene, isobutylene, and trimethylethylene as typical asymmetric oxides the author has investigated the action of ammonia on them. As a general result it was found that the hydroxyl group preferably unites with the atom of carbon to which the least hydrogen is attached.

No. 6, February 10, 1908.

Alcoholysis of Linseed Oil.—A. Haller.—By the fractional distillation of the ethers obtained by the action of alcohol on this oil in presence of ether four different fractions can be separated. From these fractions the following ethers can be isolated—methyl palmitate, methyl stearate, and methyl arachate. Arachic acid occurs only in very small quantities in the oil.

New Series of Ammoniacal Ferric Salts in which the Iron is Masked.—P. Pascal.—When ammonia is added to a solution of ferric pyrophosphate the liquid is coloured red, and a crystalline precipitate forms. Where the two liquids meet a layer of a red substance, with light yellow masses above it, can be detected, and in the upper part of the liquid long silky crystals are formed. All these substances are ammoniacal ferric salts in which the iron is masked. The crystalline precipitate contains sodium pyrophosphate, precipitated by the ammonia, and varying proportions of ammonia and iron. The ratio of the iron to the ammonia is fixed, and when excess of ammonia is present the precipitate may be regarded as formed of a combination of sodium phosphate and ferric pyrophosphate of formula $n(P_2O_7Na_4.10H_2O) + Fe_2(P_2O_7)_3Na_6 + 3NH_3 + pH_2O$. For n and p the author has obtained the following values :— $n_1 = 4$, $p_1 = 8$; $n_2 = 2{\cdot}5$, $p_2 = 15$; $n_3 = 18$, $p_3 = 25$. When the liquid is only slightly alkaline the yellow precipitate may be represented by the formula $n(P_2O_7Na_4.10H_2O) + Fe_2(P_2O_7)_3Na_6 + 2NH_3 + pH_2O$, in which n and p have the following values :—$n_1 = 18$; $p_1 = 50$; $n_2 = 9$, p_2 60. The red substance appears to have the formula $(P_2O_7)_3Fe_4 + 2P_2O_7Na_4 + 4NH_3 + 68H_2O$. When left for a long time in dry air it loses water and ammonia, and forms a brick-red powder, soluble in water, of formula $5[(P_2O_7)_3Fe_4 + 2P_2O_7Na_4] + 4NH_3 + 160H_2O$.

Magnesium Silicide. — Paul Lebeau and Robert Bossuet.—The metallo-graphic examination of silicon compounds of magnesium seems to show that only one magnesium silicide exists containing less than 40 per cent of silicon. To prove this, the authors isolated the crystals of the silicide by eliminating the magnesium as magnesium organic compound, and determined the amount of magnesium and silicon they contain. The results obtained agree closely with the formula $SiMg_2$. Thus the direct action of magnesium on silicon leads to the formation of only one definite compound, having the formula $SiMg_2$. This compound crystallises in the magnesium, but can be separated by removing the metal as magnesium organic compound. This silicide of magnesium is completely dissociated *in vacuo* or in a current of hydrogen at 1200°.

Physical Modifications of Gelatin in presence of Electroiytes and Non-electrolytes.—J. Larguier des Bancels.—In presence of various neutral salts gelatin dissolves in water at the ordinary temperature. Different neutral salts have very different solvent powers on gelatin. At the same concentration the salts of divalent metals have more solvent power than those of monovalent metals. The nitrate of a metal has a more energetic action than the chloride. In presence of electrolytes gelatin dissolves in mixtures of certain non-electrolytes and water, *e.g.*, in mixtures of alcohol or acetone and water. Other things being equal, these mixtures are more favourable to solution than pure water. A minimum quantity of pure water must be present, but when once this quantity has been reached the gelatin dissolves more rapidly the more non-electrolyte there is in the mixture. In order to separate the dissolved gelatin it is only necessary to eliminate the salts introduced into the liquid.

Rapid Determination of Potassium Bichromate in Milk. — M. Gouère. — The method depends upon the following reactions :—

$$K_2Cr_2O_7 + 6KI + 14HCl = Cr_2Cl_6 + 8KCl + 3H_2O + 6I.$$
$$2S_2O_3Na_2 — 5H_2O + I_2 = S_4O_6Na_2 + 2NaI + 5H_2O.$$

The milk is dried and ignited, the ash is taken up with water and potassium iodide, and pure hydrochloric acid are added. Then titrated hyposulphite is added until only a faint blue coloration is seen, without any tinge of yellow.

Preparation of Dithymol. Action of Bromine on Dithymol.—H. Cousin and H. Hérissey.—By dissolving thymol in alcohol, adding water and filtering, and then adding a solution of ferric chloride, a precipitate of dithymol is formed. It may be purified by re-crystallising from alcohol at 60°. When hydrated dithymol is suspended in chloroform and the theoretical quantity of bromine is added, a dibromo compound, $C_{20}H_{24}Br_2O_2$, is obtained in the form of pale yellow prismatic crystals. If this dibrominated compound is dissolved in chloroform and more bromine is added, a quinone corresponding to the dibromo-compound is precipitated by the addition of alcohol to the solution.

γ-Oxytetrolic Acid.—M. Lespieau and M. Viguier.—γ-Oxytetrolic acid, $CH_2OH—C\equiv C—CO_2H$, is a white crystalline compound prepared by adding propargyl alcohol to ethyl magnesium bromide, avoiding too great a rise of temperature. When the evolution of ethane has ceased carbon dioxide is passed in, and finally hydrochloric acid and ether are added. The raw product is purified by dissolving it in boiling benzene, from which it crystallises on cooling. The addition of bromine to this acid dissolved in ether gives an acid of formula $CH_2OH—CBr=CBr\ CO_2H$, and a lactone, $CH_2—CBr=CBr—CO$ (with an O bridge).

Action of Alcohols on Sodium Benzylate.—Marcel Guerbet.—Ethyl and propyl alcohols condense with sodium benzylate, giving benzyl ethyl and benzyl propyl alcohols respectively, $C_6H_5—CH_2—CH_2—CH_2OH$ and $C_6H_5—CH_2—C_3H_6OH$, and the acids resulting from the oxidation of these alcohols. Benzyl alcohol, on the other hand, when heated with its sodium derivative does not give phenyl benzyl carbinol ($C_6H_5—CHOH—CH_2—C_6H_5$), but stilbene ($C_6H_5—CH=CH—C_6H_5$), dibenzyl ($C_6H_5—CH_2—CH_2—C_6H_5$), toluene, and benzoic acid. Probably, however, phenyl benzyl carbinol is first formed, and afterwards decomposes into stilbene and dibenzyl.

Method of Preparing Cyclic Aldehydes. — M. Savariau.—The author has shown that the condensation of chloral with cyclic organo-magnesium compounds gives secondary trichlor-alcohols, which may be transformed into acid alcohols by the action of alkalis, and then into cyclic aldehydes :—

$$C_6H_5—MgBr \rightarrow C_6H_5—CHOH—CCl_3 \rightarrow C_6H_5—CHOH—CO_2H.$$
$$\rightarrow C_6H_5—CHO.$$

Moreover the trichlor-alcohols can be directly decomposed into aldehydes and chloroform by boiling with alkaline carbonates :—

$$C_6H_3(CH_3)_2—CHOH—CCl_3 = CHCl_3 + C_6H_3(CH_3)_2—CHO.$$

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xli., No. 2, 1908.

Reaction between Phenols and Phosphorus Pentachloride.—W. Autenrieth and Alfred Geyer.—When three molecules of phenol, cresol, or β-naphthol and one molecule of phosphorus pentachloride react together, hydrochloric acid is evolved, and a phosphorous ester dichloride of general formula $Cl_2P(OR)_3$ is obtained, according to the equation $Cl_2PCl_3 + 3HO.R = Cl_2P(OR)_3 + 3HCl$. These phosphite dichlorides are comparatively stable in absence of moisture. Water decomposes them into the phosphoric ester of the phenol and hydrochloric acid, $Cl_2P(OR)_3 + H_2O = 2HCl + OP(OR)_3$.

Ammonium Syngenite.—J. D'Ans.—In order to determine whether ammonium syngenite contains one molecule of water or two, the author subjected the pure salt to a pressure of some thousand atmospheres in a hydraulic press, thus freeing it almost entirely from its mother-liquor. The salt was then powdered, and again pressed between filter-paper. When dried in a desiccator it gave up 80 per cent of water. At 170° it gave up 6·02 per cent of water, and on ignition it lost 47·66 per cent $(NH_4)_2SO_4$. These results show conclusively that the formula is $CaSO_4.(NH_4)_2SO_4.H_2O$.

Rhodium. — A. Gutbier and A. Hüttlinger. — The authors have investigated the halogen salts of rhodium in the course of a research which has for its aim the determination of the atomic weight of rhodium. They find that sodium hexachlor-rhodiate crystallises with twelve molecules of water. Cæsium and rubidium pentachlor-rhodiates cannot be prepared by heating rhodium with cæsium or rubidium chloride in a current of chlorine, but may be obtained by decomposing the potassium salt, or by the direct union of soluble rhodium dichloride with the alkaline chloride. They are slightly soluble in water and contain one molecule of water. Potassium pentabrom-rhodiate can be prepared by heating a mixture of very finely-divided rhodium and potassium bromide in a current of bromine. The decomposition of a solution of this bromo-salt with ammonium, cæsium, or rubidium bromide yields the corresponding brom-rhodiate. These bromo-salts contain no water. The potassium and ammonium salts are fairly soluble in water, the cæsium and rubidium salts are difficultly soluble. All these rhodium compounds give up their halogen as halogen hydride when they are heated in a current of hydrogen.

Colorimetric Method of Determining the Molecular Weight of Carbohydrates. — Leonhard Wacker.—*p*-Phenylhydrazine sulphonic acid and other hydrazines possess the property of giving a red soluble derivative with the aldehydes and alcohols of the aliphatic series in aqueous solution or suspension in presence of air and of an excess

of caustic alkali. The colour of the derivative varies very little with different carbohydrates, and it has been found that the intensity of the coloration of molecular weights is constant; *i.e.*, the intensity decreases as the molecular weight increases. The velocity of the reaction is inversely proportional to the molecular weight, and is proportional to the concentration. If the red coloration appears instantly, aldehydes of low molecular weight are present. With polyatomic alcohols and carbohydrates the colour appears after about fifteen minutes. Concentrated solutions of acetone, lactic, and citric acids, urea, and albuminoids also give the reactions.

Barium Percarbonate.—R. Wolffenstein and E. Peltner. — When carbon dioxide acts upon an excess of barium dioxide the gas is absorbed, and barium percarbonate results according to the equation $BaO_2 + CO_2 = BaCO_4$. When more carbon dioxide is passed in, hydrogen peroxide is rapidly evolved, and the percarbonate is decomposed as shown by the equation $BaCO_4 + H_2O + CO_2 = BaCO_3 + H_2O_2 + CO_2$ Probably the bicarbonate, $Ba<^{HCO_4}_{HCO_3}$, is formed as an intermediate product. Thus the formation of hydrogen peroxide from barium peroxide takes place in two stages. Barium percarbonate is a light yellow substance which decomposes when warmed and when allowed to stand in air. With dilute acids it gives hydrogen peroxide, and hence it is in all probability a true salt of percarbonic acid.

Percarbonic Acid Salts.—Richard Wolffenstein and Erich Peltner.—The authors have prepared four sodium salts of percarbonic acid:—Sodium dioxide carbonate, Na_2CO_4; sodium dioxide bicarbonate, $Na_2C_2O_6$; sodium trioxide carbonate, Na_2CO_5; sodium trioxide bicarbonate, $NaHCO_4$. Sodium dioxide carbonate is prepared by the action of carbon dioxide on sodium dioxide hydrate at a low temperature. It loses oxygen rapidly even in a desiccator and attempts to re-crystallise it have not as yet been successful. The bicarbonate of sodium dioxide results when Na_2CO_4 is saturated with carbon dioxide. It is considerably more stable than the carbonate. The third salt, sodium trioxide carbonate, is obtained when carbon dioxide acts upon sodium trioxide hydrate. This hydrate has already been described by Tafel under the name natryl hydrate, and is formed when alcohol acts upon sodium peroxide, $C_2H_5OH + O{:}Na.ONa = C_2H_5.ONa + O{:}Na.OH$. Prolonged action of carbon dioxide upon natryl hydrate gives the bicarbonate, $NaHCO_4$. All these salts are exceedingly easily decomposed by water. They behave like true percarbonic acid salts, and not like carbonic acid salts with hydrogen peroxide of crystallisation.

Action of Carbonates on Tetrathionates. — A. Gutmann.—The author has already shown that with dilute alkalis tetrathionates give thiosulphates and sulphites. Hence it was to be expected that when tetrathionates are boiled with carbonates or ammonia decomposition would occur in the same way. This, however, is not the case, thiosulphate and sulphate being formed, with evolution of carbon dioxide. Very small quantities of sulphite result with sodium carbonate but not with potassium carbonate. Sulphide is never formed. The reactions occur according to the equations $4S_4O_6Na_2 + 5CO_3Na_2 = 7S_2O_3Na_2 + 2SO_4Na_2 + 5CO_2$ or $4S_4O_5 = 7S_2O_2 + 2SO_3$.

Platinum Blue.—K. A. Hofmann and G. Bugge.—Platinous chloride-dis-acetonitrile, $Cl_2Pt(CH_3{\cdot}CN)_2$, gives with silver nitrate solution a precipitate of silver chloride and an intensely blue coloured solution. The coloured product of this reaction has now been isolated and has been identified as platinous acetamide, $Pt(NH{\cdot}CO{\cdot}CH_3)_2{\cdot}H_2O$.

Reactions of Mercury Cyanide.—K. A. Hofmann and H. Wagner.—According to many observers mercury cyanide does not conduct an electric current in aqueous solution, gives no mercury oxide with caustic potash, and no silver cyanide with silver nitrate. The authors have found, however, that although it gives no, or very few, ions in aqueous solution it does react with silver salts, *e.g.*, the acetate or nitrite. With caustic potash it yields a compound $(Hg_2Cy_2)_2{\cdot}KOH{\cdot}H_2O$, which is very soluble in water, and from which silver nitrate at once precipitates pure silver cyanide.

MISCELLANEOUS.

Society of Dyers and Colourists. Award of the Perkin Medal.—At the Annual Meeting of the Society, to be held in the Hall of the Technical College, Bradford, on Friday, April 3rd, 1908, at 4.30 p.m., an Address will be given by the President, Prof. Raphael Meldola, F.R.S., F.I.C., on "The Founding of the Coal-tar Colour Industry." Prof. Meldola, who is a Past-President of the Chemical Society, was elected by the Council to the Presidency of the Society upon the death of the late Sir William H. Perkin. At the same meeting the first awards of the Perkin Medal will be made to Prof. Graebe and Prof. Liebermann for their "Synthesis of Alizarin, 1868." The Perkin Medal, which will be awarded once in each successive period of from three to five years, has been established as a recognition of investigations, discoveries, or inventions of high scientific or industrial importance applicable to or connected with the tinctorial industries.

The British Association, Winnipeg Meeting.—The Council of the British Association for the Advancement of Science has nominated Prof. J. J. Thomson, F.R.S., Cavendish Professor of Experimental Physics in the University of Cambridge, to be President of the meeting of the Association which is to be held at Winnipeg next year. The investigations carried on by Prof. Thomson in the Cavendish Laboratory, and by the distinguished men of science who first worked under him and received inspiration from his researches, laid the foundation for the new views held by chemists and physicists as to the electronic constitution of matter and the remarkable properties of radio-active substances. In 1894 Prof. Thomson was awarded one of the Royal Medals of the Royal Society, and to this was added, in 1902, the Hughes Medal, in recognition of his contributions to the advancement of electrical science, especially in connection with the phenomena of electric discharge through rarefied gases. Two years ago he was the recipient of the Nobel Prize for Physics. It is understood that provision will be made by the Canadian Government, in the estimates for the coming financial year, for a grant of 25,000 dollars (£5000) by the Dominion Parliament towards the expenses of the Association's visit to Winnipeg. The City of Winnipeg itself proposes to make a grant of 5000 dollars (£1000). The week of the meeting will probably be from August 25th to September 1st, 1909.

MEETINGS FOR THE WEEK.

Monday, 23rd.—Royal Society of Arts, 8. (Cantor Lecture). "Fuel and its Future," by Prof V. B. Lewes.

Tuesday, 24th.—Royal Institution, 3. "The Egyptian Sudan—its History, Monuments, and Peoples, Past and Present," by E. A. Wallis Budge, M.A., &c.

—— Royal Society of Arts, 4.30. "The Mineral Resources of Western Australia," by the Hon. C. H. Rason.

—— Faraday Society, 8. Presidential Address, "Some Aspects of the Work of Lord Kelvin," by Sir Oliver Lodge.

Wednesday, 25th.—Royal Society of Arts, 8. "Recent Improvements in Decorators' Materials," by A. S. Jennings.

Thursday, 26th.—Royal Institution, 3. "Standardisation in various Aspects—(2) Electrical Engineeering," by R. T. Glazebrook, F.R.S., &c.

—— Royal Society of Arts, 8. (Howard Lecture). "The Navigation of the Air," by H. S. Hele-Shaw, F.R.S., &c.

Friday, 27th.—Royal Institution, 9. "Radio-active Change in the Earth," by Hon. R. J. Strutt, F.R.S., &c.

—— Physical, 5. (At the Northampton Polytechnic Institute, Clerkenwell). "Notes on the Plug Permeameter," "Use of Shunts and Transformers with Alternate Current Measuring Instruments," "Wattmeters," by C. V. Drysdale.

Saturday, 28th.—Royal Institution, 3. "Electric Discharges through Gases," by Prof. J. J. Thomson, F.R.S.

THE CHEMICAL NEWS.

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NEO-ERBIUM.

By K. A. HOFMANN and O. BURGER.

The decomposition of the old erbium earth carried out by Marignac (*Archives Genève*, 1878, lxiv., 87), Nilson (*Ber.*, 1880, 1430), and Cleve (*Comptes Rendus*, 1879, lxxxix, 708, and xci., 382), led to the separation of the accompanying elements: scandium, ytterbium, thulium, and holmium from erbium proper, Cleve's neoerbium. Krüss and Nilson (*Ber.*, 1887, 2134) questioned the elementary nature of this substance with atomic weight $R^{III} = 166{\cdot}25$, because they found that according to its mineralogical origin the earth exhibited a relative intensity of the absorption bands which varied within wide limits.

But, as it is now known (Muthmann and Stützel, *Ber.*, 1899, xxxii., 2653; Forsling, *Bih. Sv. Akad. Verb.*, xviii., 1, 4) that the presence of several absorbent or even colourless constituents exercises an influence which cannot be controlled on the relative strengths of the bands and lines, such reasons can no longer hold good. Nevertheless more recently (*Zeit. Anorg. Chem.*, 1893, iii., 369) Krüss, by fractional precipitation with aniline, separated an almost pure erbium preparation, obtained by Nilson, into earths of different equivalent weights, and hence he concluded "that we are not justified in regarding erbium earth as a single oxide Er_2O_3."

We have worked up Nilson and Krüss's material in order to find out definitely how far the decomposition could be carried, and in order to get a preparation which would be as simple as possible and in which the most interesting property of this class of substance, namely, the selective absorption and emission of light, would appear simpler than before.

It was found that the neo-erbium earth obtained by Nilson and Cleve's method still contained impurities, which, however, for the most part appeared to be thulium, holmium, and dysprosium. By the further purification described below the atomic weight was raised from the value $R^{III} = 166{\cdot}25$, previously obtained, to 167·43, and the absorption spectrum was simplified. Nevertheless the earth showed no indication of decomposition in Krüss and Nilson's sense of the word, although separating agents were tried which otherwise are exceedingly effective.

The spectra of the pure earth will be described at the end of this article.

Amongst methods of purifying, fractionation with aniline hydrochloride (Krüss, *Zeit. Anorg. Chem.*, 1893, iii., 353) was rejected, after it had been found that the removal of holmium could not be effected thus. For this purpose treating the salt with concentrated potassium sulphate solution was best; from the easily soluble parts the holmium lines 640 and 536 disappeared almost entirely, and the samarium lines completely. The removal of strongly basic earths was effected by the evaporation of nitrate solutions with excess of sodium nitrite to dryness on the water-bath. When the residue was taken up with water most of the erbium hydroxide was left. In this respect erbium resembles thorium (*cf.*, Erdmann, *Lehrbuch*, 1902, 603), although in other analytical properties they are not alike.

After the rest of the terbium earths had been removed with the difficultly soluble parts by the partial crystallisation of the formate, the arc spectrum, taken by Prof. G. Eberhard, revealed only small quantities of thulium, neo-holmium, and dysprosium, besides traces of yttrium and ytterbium. By very gradual fractional precipitation with dilute ammonia it was possible to remove the absorption lines of thulium entirely, and thus to exclude also the traces of ytterbium.

To separate dysprosium and neoholmium the method suggested by Urbain (*Comptes Rendus*, cxlii., 785), the partial crystallisation of the ethyl sulphates was very useful. The easily soluble crystals of the mother-liquor contained no more dysprosium, and showed traces of holmium lines only in very concentrated nitrate solutions. The crystals and liquor were identical as regards spectrum and equivalent weight.

Although the methods of fractional precipitation with ammonia, decomposition of the nitrites and partial solution in ammonium carbonate (C. James, Chemical News, xcv., 181) were repeatedly applied to this material, there was no indication of any further decomposition. The method of separating the yttrium earths, discovered by Auer v. Welsbach (*Monatshefte*, 1906, xxvii., 942), by the crystallisation of the ammonium double oxalate, is, as we can show, exceedingly effective for separating holmium and erbium. Our material behaved like a single substance.

After all impurities had been removed by ordinary reagents for purifying—sulphuretted hydrogen, ammonia, oxalic acid—we determined the equivalent weight by the sulphate method, observing the precautions enumerated by B. Brauner (*Proc. Chem. Soc.*, xvii., 63; and *Journ. Chem. Soc.*, lxxxi., 1243). For vessels we used platinum crucibles of perfectly constant weight, and heated them in electric resistance furnaces. Further orientation experiments led to similar results to those which Brill (*Zeit. Anorg. Chem.*, xlvii., 464) had obtained with different rare earths by means of a micro-balance.

The normal composition of the sulphate was reached very slowly at 400°, quickly at 475°, and lasted to 630°. Constant weight was reached in the shortest time at 580°. The oxide was weighed before being converted into sulphate and after decomposition of the sulphate at 1100°, which gave an accurate control against loss.

At 850° a second stopping point in the composition of the sulphate appeared, corresponding to the basic salt, $(ErO)_2SO_4$; it did not, however, appear sharp enough for an equivalent weight determination.

	Oxide (grms.).	Sulphate (grms.).
I.	0·9048	1·4724
II.	0·4666	0·7594
III.	1·4181	2·3077
IV.	1·0789	1·7563

Hence, assuming that the metal is trivalent, the following atomic weights are obtained:—

I.	167·43
II.	167·37
III.	167·43
IV.	167·28

I. and II. correspond to the mother-liquor and the last crystals from the treatment with ethyl sulphate by Urbain's method; III. and IV. correspond to the limits of the ammonium oxalate fractionation, III. belonging to the easily soluble crystals, and IV. to those which dissolve with difficulty.

The most trustworthy numbers, because they were obtained with the purest material (*cf.* the spectra), are I. and III., which agree perfectly, viz., $R^{III} = 167{\cdot}43$ ($O = 16$, $S = 32{\cdot}06$).

(Both in the crystallisation of the ethyl sulphates and of the ammonium double oxalates the impurities holmium and dysprosium, which are most difficult to remove, go into the first crystals).

In Abegg's new "Handbuch der Anorganischen Chemie" (1906, III., i., 318), B. Brauner states that with an erbium obtained from Cleve he found $Er = 167{\cdot}14$, while Cleve himself gave $Er = 166{\cdot}25$. The specific weight of the earth, obtained by igniting the sulphate at 1100°, was found to be 8·616 at 15°.

The absorption spectrum of the 10 per cent nitrate solution, after a two-minute exposure, using a layer 1·5 cm. thick, was taken on a panchromatic plate.

It must be stated that $\lambda = 653$ appears clear to the eye, and that, especially in concentrated solutions, $\lambda = 667$ and $\lambda = 541$ are also visible. In the ammonium carbonate solution two lines, $\lambda = 657$ and $\lambda = 653$, are situated in the red.

Comparison of Forsling's measurements (*Bih. Sv. Vet. Akad. Handl.*, xxiv., I., 7) with Cleve's neoerbium shows that in our preparation the lines 648, 549, and probably also 453 are missing; yet there is no decomposition in Krüss (*Ber.*, 1887, xx., 3067) and Nilson's sense of the word, because the lines ascribed by them to $Er\alpha = 653$ and $Er\beta = 523$ remain without perceptible alteration of intensity.

The oxide, prepared like an incandescent mantle, shows very interesting optical properties. In the heat of a Bunsen burner emission bands appear on continuous back-grounds; the position of these bands agrees fairly well with the absorption spectrum of the nitrate solution.

But if the concentrated crater light of an arc lamp is allowed to fall on the oxide through a quartz lamp, very many sharp absorption lines appear; in groups they cover the absorption region of a concentrated nitrate solution, and represent the reversal of the emission bands. In the red we counted between $\lambda = 669$ and $\lambda = 646$ nine lines, the strongest of which lay at 661, 653, and 651. Between $\lambda = 565$ and $\lambda = 518$ eleven lines were measured, of which the following were the most marked :—540, 525, 524, 521, 519, 518. The absorption lines between $\lambda = 495$ and $\lambda = 490$ were less numerous, viz., three; between $\lambda = 463$ and 445 two are easily seen.

The accurate measurements of this beautifully sharp spectrum, as well as experiments on changes in the magnetic field, will be reported elsewhere.

As Bauer (*Ber.*, 1901, xxxiv., 2460) and Marc showed, the pure earths do not emit a discontinuous light if they are exposed to cathode rays. Cathode luminescence appears if a solid solution of a coloured earth in a colourless earth is present. As the amount of coloured earth is increased the luminescence is gradually extinguished. Thus our oxide in comparison with the surrounding gas and with interspersed tungstate remained dark in the cathode tube.—*Berichte*, 1908, xli., 308.

DETERMINATION OF COCOANUT OIL IN BUTTER.

By G. R. THOMPSON, F.I.C., and ARNOLD R. TANKARD.

The results obtained by Mr. T. R. Hodgson with the oxidation process recently devised by him for the determination of cocoanut oil in butter, and published in the Chemical News (vol. xcvi., pp. 273, 288, 297) were so startling that, in view of the need for an accurate method for this purpose, we immediately submitted his process to a critical examination in this laboratory. The conclusions we then formed (in January last) are confirmatory in all respects of those given by Messrs. Ross and Race (Chemical News, vol. xcvii., p. 110), and prove the method to be valueless.

We first subjected one sample each of genuine butter, a vegetable butter substitute (largely cotton-seed oil) and cocoanut oil to the new method, and side by side with these samples ran a blank experiment with the alcoholic potash and other reagents employed. The following results were obtained, the procedure being strictly as detailed by Mr. Hodgson, using standard ferrous ammonium sulphate solution in the final titration :—

Sample.		N/10 $KMnO_4$ used. Cc.	= Oxygen equivalent.
Butter	*a.*	34·95	139·8
	b.	35·30	141·2
Butter-substitute	*a.*	35·75	143·0
	b.	36·70	146·8
Cocoanut oil	*a.*	37·70	150·8
	b.	38·00	152·0
Blank experiment on reagents		31·60	(126·4)

It will be seen that these figures fail to show that differentiation between the various samples, such as was obtained by Mr. Hodgson; further, the blank experiment itself showed a very considerable absorption of permanganate, and this caused us no surprise, for the destruction of the permanganate, even in the absence of fatty acids, is obvious during the operation. On heating quantities of standard potassium permanganate solution direct, at 100° C., with water and the sulphuric acid (50 per cent) as prescribed in the method, we obtained the following results amongst others :—

	N/10 $KMnO_4$ taken. Cc.	$KMnO_4$ left after heating. Cc.
1	50·0	14·2
2	25·0	7·0

It occurred to us that perhaps "50 per cent" (sulphuric acid) was an error for "5 per cent," and we therefore determined to what extent the weaker acid destroyed the permanganate solution. We found that even with 5 per cent sulphuric acid a decinormal solution of potassium permanganate is appreciably attacked. For example, in a typical instance 1·0 cc. N/10 $KMnO_4$, out of 50·0 cc. employed, disappeared after heating for thirty minutes at 100° C. with 50 cc. of 5 per cent sulphuric acid and 20 cc. of water.

There can be no doubt, therefore, that Mr. Hodgson's process is fundamentally unscientific and based upon error. We wish to add that, although we have written to Mr. Hodgson on two occasions (the first letter being despatched on January 18th last), pointing out the results of our experiments with his method, we have not received any reply from him up to the present time, hence this present communication.

County Analyst's Laboratory, Newport, Monmouthshire.

THE ATOMIC WEIGHT OF CHLORINE.*

By WILLIAM A. NOYES and H. C. P. WEBER.

(Continued from p. 137).

Method of Carrying out the Determinations. First Series.

There are three parts to the apparatus, which was prepared for a determination in the following way :—

The Palladium Tube.—This consisted of a cylindrical tube with a stopcock sealed on at each end. The tube at one end was bent downwards at right angles and drawn out to a tip at B. Connection with the hydrogen generator was made by sealing the tip into a corresponding socket with Khotinsky cement. The three-way stopcock at B was opened in the position so that the small amount of air in the limb of B was swept out. Communication was then established between the palladium and the hydrogen generator, and hydrogen was led in until no more was was absorbed. The stopcock at A was next opened, and the hydrogen allowed to sweep through the apparatus for a short while. The stopcocks were then closed, and after cleaning the apparatus it was ready for weighing. Before the apparatus was used the first time, it was repeatedly charged with hydrogen and the hydrogen driven out at 400°. After that the tube was ready for charging anew at the end of each experiment.

Chlorplatinate Tube.—This tube had the general form as shown in the diagram (Fig. 2). The potassium chlorplatinate was introduced through the curved neck which was open at D. For this purpose the hard glass tube in which the chlorplatinate had been heated to 400° was connected to it by a short piece of stout rubber tubing and the chlorplatinate was shaken into the apparatus. The end D was then sealed off without allowing vapours from the flame to enter the tube. After this was done the

* From *The Journal of the American Chemical Society*, xxx., No. 1.

apparatus was attached to the Sprengel pump and evacuated to a few thousandths of a millimetre at a temperature of 350°. This temperature was maintained for about four hours. After closing the stopcock, disconnecting and rinsing after it was cool, the apparatus was transferred to the desiccator before weighing.

Absorption Tube for the Hydrochloric Acid.—This consisted of a bulb having a volume of about 100 cc. It terminated in two tubes with stopcocks and sockets to fit the tips of the two tubes from the platinum apparatus at E. Fifty cc. of boiled distilled water were poured into this bulb. It was then evacuated by means of the Sprengel pump, which was protected by an extra phosphorus pentoxide tube in this case. The evacuation was continued as long as air could be removed from the apparatus or liquid. Usually it was found necessary to allow the partly evacuated apparatus to stand for a day before the discovered. After the three parts of the apparatus had thus been connected with each other and with the vacuum pump, the connections were evacuated. The gas in the two connecting limbs at E was removed by opening the stopcocks at F and pumping the gases out over the chlorplatinate, which had meanwhile been brought to a temperature of about 300°. When every part of the apparatus had been evacuated to a few thousandths of a millimetre, as shown by the McLeod gauge attached to the pump, connection with the pump was cut off. The stopcock of the hydrogen apparatus at B was then opened and gradual heating of the hydrogen tube commenced. Then the stopcock at C was opened very gradually and the hydrogen admitted to the chlorplatinate. Next, the four stopcocks communicating with the absorption tube were opened. This was done very gradually to prevent a sudden rush of gas into the absorption tube and consequent carrying over

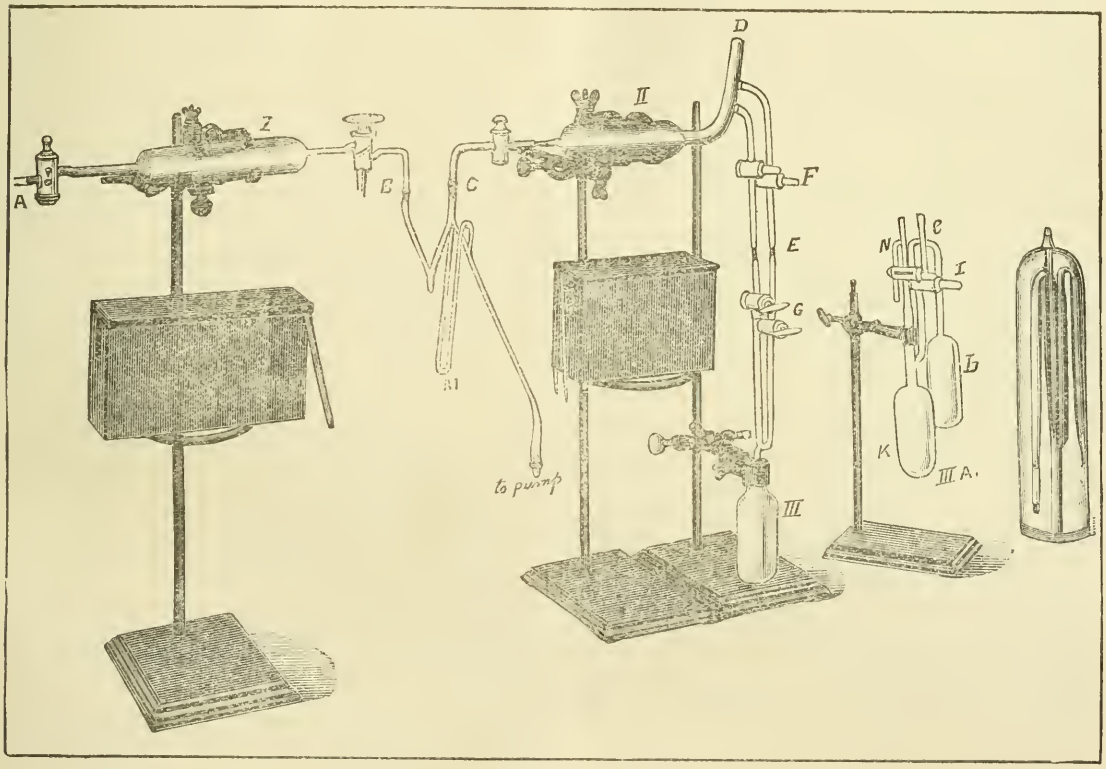

Fig. 2.

last traces of air could be removed from the water. After evacuation the apparatus was rinsed and set in the desiccator for weighing. Then, the different portions of the apparatus having been weighed, they were set up as shown in Fig. 2. The potassium chlorplatinate and the palladium charged with hydrogen were enclosed by electrically heated air-baths. These are lowered in the diagram to show the apparatus.

The tip B of the hydrogen tube and C of the chlorplatinate tube were connected with each other and with the Sprengel pump by means of a T-tube. The two tips from the chlorplatinate tube were connected to the two corresponding sockets of the absorption tube. These joints were made with Khotinsky cement. (P. G. Nutting, of this Bureau, has supplied us with a cement of the same character, which seems to answer the purpose as well as the Khotinsky. It is made by fusing together equal parts by volume of rosin and pure rubber).

The joints were perfectly tight and no leakage was ever

of the finely divided potassium chlorplatinate. In doing this, the stopcocks were opened in such order that communication was first established through the tube entering the chlorplatinate apparatus at the lower level. Following this, communication was established by means of the adjoining tube. The purpose of the double connection between the chlorplatinate and the absorption tube was to prevent stagnation of the gas current between the two parts of the apparatus. A little hydrogen was always carried along with the hydrochloric acid toward the absorption apparatus. This would tend to accumulate and block the current. By making the level of the second tube somewhat higher than that of the first, the tendency of the hydrogen to rise would cause a direct and continuous flow. Actually, this arrangement proved entirely satisfactory.

The apparatus remainded in this condition for several hours. The temperature of the palladium tube generating the hydrogen was allowed to rise slowly at such a rate

that the pressure in the apparatus was kept at or below one atmosphere. This pressure was measured by means of a small mercury manometer M which formed a part of the connecting T-tube B C. The closed end of the manometer contained a little air. By this means it was possible to measure any pressure from zero to more than one atmosphere with a light manometer 8—10 cm. in length.

When it was deemed that a sufficient quantity of hydrogen had been evolved from the palladium tube the stopcock B of this part of the apparatus was closed and the palladium allowed to cool off. The temperature of the tube containing the chlorplatinate was allowed to rise to 350°. At the same time the absorption tube, which had been cooled by ice during the earlier part of the experiment was now cooled to −20° by a mixture of ice and dilute sulphuric acid. The hydrogen remaining in the apparatus upon cutting off the palladium tube was continuously converted into hydrochloric acid and removed as such by the water. This could be followed by means of the manometer M previously mentioned. After two or three hours the manometer had reached the lowest point which it would indicate. At this point the stopcocks G of the absorption tube were closed. The conditions prevailing at this moment were as follows:—

The chlorplatinate tube still contained an excess of potassium chlorplatinate and was at a temperature of 350°.

The absorption tube was at a temperature of −20°. The residual pressure throughout the apparatus was very low.

Under these conditions but a very minute quantity of hydrogen could have escaped conversion into hydrochloric acid. To determine this, connection with the Sprengel pump was again established, and that part of the apparatus between the stopcock B of palladium tube and the stopcocks G of the absorption tube was evacuated to the best vacuum obtainable by the pump, usually a few thousandths of a millimetre. The gas pumped out was collected in a eudiometer and analysed. In analysing the gases their volumes were read at a pressure of about one-sixth to one-seventh of an atmosphere, making accurate determination possible. Thus the volume of 1 cc. under these conditions represented less than 0·02 mgrm. of hydrogen.

The residual gas having been pumped out of the apparatus, all stopcocks were closed and the apparatus taken apart. All traces of the cement adhering to the glass where the various pieces had been joined were carefully removed. The pieces were then rinsed with distilled water, when sufficiently cool, wiped dry and transferred to the desiccator. The following day they were weighed. The determination itself required about eight hours, of which about two hours were used for the evolution of hydrogen and about three hours for the pressure to drop from atmospheric to practical zero.

Second Series.

Before giving the results obtained by the first series it may be just as well to turn to the manipulations giving the second set of values. They are essentially the same as in the first series with this difference: the hydrochloric acid generated was condensed as a solid by cooling with liquid air and connection with all other parts of the apparatus was cut off before it was absorbed by water. The point in view was this: During the period of absorption of the hydrochloric acid it might be possible that a transfer of water would take place from the absorption apparatus to the chlorplatinate apparatus and remain there in spite of the fact that there was not only a difference of 370° in temperature between the two parts but also a very high vacuum. This would cause the apparent amount of chlorine transferred to appear lower than the real. Or there was the possibility of the water vapour reacting with the material in the chlorplatinate tube. To eliminate these possibilities the reaction was so carried on that the chlorplatinate was at no part of the determination in contact with water vapour.

Further, this series differs from the first in that the hydrogen used was generated from a solution of barium hydroxide, the hydrogen in the first series being obtained from a sulphuric acid electrolyte. The absorption apparatus in the second series (which simply took the place of the water absorption tube) was constructed as follows:—

The bulb K was designed for the condensation of the hydrochloric acid and had a volume of 100 cc. It terminated in a neck from which led two exit tubes provided with the stopcocks H and I. The stopcock at I was provided with two perforations so that communication could be established either between the chlorplatinate tube and K or between the two bulbs K and L. The bulb L had a volume of 70 cc. and contained the water for the absorption of the hydrochloric acid. Below H a miniature mercury manometer was affixed. This was found absolutely necessary in order to follow the conditions of pressure during the transfer of the solid hydrochloric acid in K to the water in L. Indeed, previous to the attachment of this device to the apparatus every determination was lost either by the bursting of the apparatus or the blowing out of the stopcocks. By making the air space above the mercury of capillary tubing, while the remainder was about 1½ mm. in bore, satisfactory readings could be obtained both at normal and reduced pressures, and there was no danger of the mercury being sucked out of the manometer.

To prepare the apparatus for weighing, somewhat more than 50 grms. of water were filled into L through a small opening at P. The water was then boiled, and when all air had been expelled the opening at P was sealed off. The whole apparatus was then evacuated with the Sprengel pump, the last traces of air being removed from L by opening the stopcock I momentarily until the limit of the pump was reached. Rinsing, drying, and desiccation then completed the preparations for weighing as usual. The apparatus was then put together and prepared for the determination in precisely the same manner as in the first series, with the one difference that the absorption apparatus III A was now connected at E instead of the absorption tube III. Communication with the water bulb L was entirely cut off during the first part of the determination. The condensation bulb K was plunged in liquid air at the beginning and kept at the temperature of boiling air throughout the determination.

In opening the stopcocks to obtain communication between the various parts of the apparatus very great care had to be exercised, as the first rush of gases into the chilled condensation bulb often carried some of finely divided chlorplatinate with it. In a few cases it was not possible to avoid this. Since this chlorplatinate remained in the condensation bulb K, its amount could be found at the end of the determination and a suitable correction applied.

After communication had been established between the hydrogen tube, the chlorplatinate tube, and the condensation tube, the hydrogen tube was cautiously heated so as to obtain a constant and steady rise in temperature. Somewhat more care was necessary in this series, as there seemed to be a greater tendency for the pressure in the hydrogen apparatus to fall below that of the remaining parts. This would result in the finding of hydrochloric acid in the palladium tube at the end of the experiment. Suitable corrections were made for this and will be spoken of with the other corrections. When the hydrogen tube had reached a temperature of from 150° to 160°, it was judged that the requisite amount of hydrogen had been evolved. The stopcock from the hydrogen tube was then closed. Any temperature above 150° sufficed for the reduction of the chlorplatinate by the hydrogen, but at the end the temperature of the chlorplatinate tube was run up to 400°. The condensation bulb was kept fully submerged in liquid air. After the supply of hydrogen had been turned off, the pressure in the apparatus gradually sank until all hydrogen had been used up and all hydrochloric acid condensed. The conditions then were: excess of the chlorplatinate at 350° to 400°; the hydrochloric

acid at about −180° and a small fraction of a millimetre residual pressure. The stopcocks of the condensation tube were then closed and the residual gases in the remaining parts of the apparatus pumped out.

The condensation tube was then separated from the remaining parts of the apparatus and the transfer of the hydrochloric acid to the water commenced. The water bulb L was plunged into ice water and the condensation bulb K removed from direct contact with the liquid air, but not entirely beyond the cold vapours. As soon as the pressure of the hydrochloric acid had risen to a small part of an atmosphere, communication was established with the cold water in L. After some hydrochloric acid had been absorbed by the water the bulb L was cooled by ice and dilute sulphuric acid instead of by ice alone. With the aid of occasional shaking of the absorption bulb the last of the condensed hydrochloric acid was finally absorbed by the water. With cautious manipulation the pressure in the apparatus did not rise above one-half atmosphere during the transfer and remained at a few millimetres at the close. The stopcock I between K and L was then closed, and the apparatus was cleaned, rinsed, wiped, and set aside to be weighed. The determinations of the second series required about ten hours from beginning to end. About two hours were consumed in transferring the solidified hydrochloric acid from the condensation to the absorption bulb. The solidified hydrochloric acid resembled snow in appearance and the greater part of it was absorbed by the water without passing into the liquid state. Towards the end of the transfer, when the absorption became less rapid, the remaining hydrochloric acid would liquefy attended by a sudden rise in pressure. Shaking of the absorption tube immediately reduced the pressure and caused the liquid hydrochloric acid to solidify to a glassy solid.

(To be continued).

THE USE OF TIN AS A CATHODE FOR THE RAPID QUANTITATIVE ELECTROLYTIC DEPOSITION OF ZINC, COPPER, SILVER, CADMIUM, AND NICKEL.*

By LAURENCE T. SHERWOOD and GELLERT ALLEMAN.

(Concluded from p. 139).

Silver.—When silver nitrate solution comes in contact with tin a black deposit forms on the tin. This action is, of course, objectionable; but if potassium cyanide were first added and the double cyanide formed, it did not take place. However, when potassium cyanide was used alone as an electrolyte the silver deposits were dark and loose. The addition of a suitable amount of oxalic acid afforded a reducing action, and this difficulty was also overcome, the deposit being the characteristic milk-white silver. Unless rather low currents were used the deposits had somewhat more tendency to sponginess than on platinum, but if a little clear gelatin solution were added, 1½ ampère could be used.

Potassium cyanide in the dish when no current is passing of course dissolves a small amount of tin (from 1 to 3 mgrms. if allowed to stand a minute), but when the tin surface is absolutely clean of oxide or any foreign material the dish does not lose appreciable weight in silver determinations if the circuit is closed before the addition of the cyanide. A number of experiments were made with the potassium cyanide alone in the dish, and also with the cyanide and oxalic acid together. Hot water was first put in the dish and the circuit closed, after which the respective amounts of cyanide or mixture of the two reagents that were used for the silver determinations were added. The remaining operations were the same as in the course of a regular analysis. (Table VI.).

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When silver is being deposited it is improbable that tin ever dissolves at all, for the determinations were fully as accurate as any made on the platinum dishes. To prevent possible solution of tin the following procedure was observed:—The cathode was placed upon its support and hot water added; the circuit was closed, having the rheostat adjusted so that about 1 ampère would flow when the electrolytes were introduced; oxalic acid, gelatin, and the cyanide solution of silver were added in the order named; the volume was diluted to 100 cc.; the electrodes were adjusted, the rotator started, and the current regulated. (The gelatin should be pure and the solution clear; "isinglass" was the material used). It was not thought that oxalic acid would dissolve tin appreciably when the current is not passing, except on standing. It is certain that it does not when the current is on.

There was no trouble in depositing one layer of silver upon another indefinitely if each time the loose metal were wiped out and the remaining coating well brushed, but it is probably safer not to deposit more than four or five layers without cleaning. When desirable the firm deposit may be cleaned off with potassium cyanide. The action may be hastened by passing a current of about 0·2 ampère through the cyanide, making the dish the anode. The deposit could also be scoured off without the aid of a solvent. (Table VII.).

Cadmium.—Exner's condition for cadmium applied to the tin cathode with little alteration (see *Journ. Am. Chem. Soc.*, xxv., 903). Sulphuric acid was the electrolyte, and this, of course, dissolved tin unless the dish was protected by the current. The circuit therefore had to be closed before adding the acid. Experiments showed also that only a small quantity could be used. With more than 1 cc. of acid, specific gravity 1·115 (concentrated acid diluted 1 to 10), the solvent action was more powerful than the tendency of the current to keep the metal at the cathode. But regardless of the solvent action, 1 cc. of the electrolyte gave the best deposits of cadmium. The experiments recorded in Table VIII. were made to show the solvent action of different amounts of acid of the specific gravity noted above. The dishes were filled with hot water, the circuit closed, the rotator started, and the acid added from a pipette. The regular procedure of a determination was then followed.

In the experiments of Table IX., made by Mr. Hill, all the reagents were put in the dish before the circuit was closed, except the acid, the addition of which was the final detail of the manipulation. The deposits were crystalline, closely resembling zinc. The adherent coating was cleaned out once in four or five determinations, only the loose material being removed after the other depositions. Sulphuric acid aided by a feeble current dissolved the coatings, or else they were scoured off without using any solvent.

Copper.—Copper, although usually most readily determined by electrolytic methods, presented considerable difficulty. When a solution of the neutral or slightly acid sulphate was put in a tin dish a black deposit came down. Also, with the common acid electrolytes, loose black deposits resulted in the attempt to separate the metal by a current. Additions of ammonium hydroxide to the sulphate solution prevented the immediate formation of the black coating until the current was introduced, but results from this electrolyte were not at all promising, the deposits being dark and loose.

An adaptation of E. Wagner's oxalate method gave fairly good results, although considerable manipulation was required (*Zeit. Electrochem.*, ii., 613). The dish, first of all, should be absolutely free from oxide of any sort, although a deposit may be made upon a surface of bright adherent copper. Then by observance of the following conditions good results may be obtained:—Mix in a beaker 55 cc. of saturated ammonium oxalate solution, 5 cc. of saturated oxalic acid solution, and 1 cc. clear solution of pure gelatin (1 grm. of gelatin = 1000 cc.). Place the dish on its support, introduce this mixture, start the rotator, and

Table VI.

Weight of dish.	KCN, in grms.	Saturated solution of oxalic acid, in cc.	Ampères.	Time, in minutes.	Loss of weight.
59·8008	2	10	0·6	20	—
65·1525	2	10	0·6	20	—
63·1403	2	10	0·6	20	0·0001
64·8920	2	10	0·6	20	0·0003
63·0190	2	10	1·0	20	—
61·8203	2	10	1·0	20	—

Table VII.

$AgNO_3$ = Ag, in grm.	KCN, in grms.	Oxalic acid in cc. of saturated solution.	Gelatin (1 grm. = 100 cc.), in cc.	Volume when diluted.	Approximate temperature at start.	Current, $N.D._{100}$ = A.	Volts.	Time, in minutes.	Ag deposited, in grms.	Error in per cent of Ag, in $AgNO_3$.
0·2500	2	10	1	100	65°	1·0	6·0	25	0·2500	0·00
							6·0	25	0·2499	0·02
							6·0	25	0·2503	0·08
							6·0	25	0·2501	0·03
							6·0	25	0·2497	0·07
0·2500	2	10	1	100	65°	1·5	7·0	20	0·2502	0·05
							7·0	20	0·2504	0·10
							6·5	20	0·2497	0·07
							6·0	20	0·2499	0·02
							6·5	20	0·2495	0·12
							6·6	20	0·2498	0·05

Note.—Speed of rotator in first five determinations was 700 revolutions per minute; in the last six, run by Mr. Hill, the speed was 550 revolutions per minute.

Table VIII.

Weight of dish.	H_2SO_4 (sp. gr. 1·115), in cc.	Ampères.	Time, in minutes.	Loss of weight.
62·9874	3	5	10	0·0009
64·7832	2	5	10	0·0003
62·9865	1	5	10	0·00

Table IX.

$3CdSO_4.8H_2O$ = Cd, in grm.	Volume when diluted, in cc.	Approximate temperature at start.	Current $N.D._{100}$ = A.	Volts.	Time, in minutes.	H_2SO_4 (sp. gr. 1·115), in cc.	Cd deposited, in grms.	Error in per cent Cd in $5CdSO_4.8H_2O$.
0·2500	100	65°	5	24—15	10	1·0	0·2502	0·04
						2·0	0·2495	0·09
						1·5	0·2504	0·07
						1·0	0·2503	0·05
						1·0	0·2499	0·02
						1·0	0·2501	0·02
						1·0	0·2503	0·05
						1·0	0·2500	0·00

Note.—Speed of the rotator was 550 revolutions per minute.

Table X.

$CuSO_4.5H_2O$ = Cu, in grm.	Saturated solution $(NH_4)_2C_2O_4$, in cc.	Saturated solution of $H_2C_2O_4$ at start, at 10, 15, and 18 minutes respectively.	Volume when diluted, in cc.	Approximate temperature at start.	Current, $N.D._{100}$ = A.	Volts.	Time, in minutes.	Cu deposited, in grm.	Error in per cent of Cu in $CuSO_4.5H_2O$.
0·2500	55	5+10+5+5	100	20	5	19—10	24	0·2498	0·02
							21	0·2495	0·05
							20	0·2502	0·02
							20	0·2492	0·08
							20	0·2502	0·02
							22	0·2502	0·02
							21	0·2487	0·14
							22	0·2498	0·02
							20	0·2487	0·14
							21	0·2490	0·11
							20	0·2492	0·08

Note.—Speed of the rotator was 550 revolutions per minute.

Table XI.

$NiSO_4.7H_2O$ = Ni, in grm.	30 per cent acetic acid, in cc.	NH_4OH (sp. gr. 0·90), in cc.	Volume in cc. when diluted.	Approximate temperature at start.	Current $N.D._{100}$ = A.	Volts.	Time, in minutes.	Ni deposited, in grm.	Error in per cent of Ni in $NiSO_4.7H_2O$.
							13	0·2497	0·03
							14	0·2502	0·02
							13	0·2496	0·03
0·2500	10	30	100	65°	5	9	13	0·2500	0·00
							13	0·2504	0·03
							13	0·2491	0·08
							13	0·2495	0·04
							13	0·2501	0·01

Note.—Speed of rotator was about 700 revolutions per minute.

Table XII.

	$(NH_4)_2SO_4$, in grms.								
							15	0·2500	0·00
0·2500	1·5	25	100	65°	5	18—10	15	0·2497	0·03
							16	0·2504	0·03
							15	0·2500	0·00

Note.—This series was run by Mr. Hill. Speed of the rotator was about 550 revolutions per minute.

add the copper sulphate solution. Without delay close the circuit and dilute to a suitable volume. At the end of ten minutes add from a pipette 10 cc. of oxalic acid solution, at fifteen minutes add 5 cc., and at eighteen minutes 5 cc. The deposition will then usually be complete after twenty minutes. The solution must be cold at the start, for otherwise the deposit will be black and loose. It is important too that the anode be rotating when the copper solution is added, since occasionally a very adherent blue material formed on it which could not be washed off. If the oxalic acid was not added at the stated times the results were invariably low, slight amounts of copper remaining in solution until the end of about thirty minutes. The deposits were dark red and crystalline, but adherent enough to wash and weigh. They were removed by a hot potassium cyanide solution. Series X. was run by Mr. Hill.

This method, while fairly accurate if the conditions are closely observed, requires more manipulation than the methods on platinum. It was observed, too late for an investigation to be undertaken, that from cyanide solutions copper, with a high current density, comes down on tin as a bright and extremely adherent deposit just as it does on platinum. Since the cyanide was a satisfactory electrolyte for the quantitative determination of silver on tin, it is quite probable that it may also be used for copper. A thesis written in 1906 by Miss Anna L. Flanigan at the University of Pennsylvania describes some recent cyanide methods for copper deposition on platinum, and it is intended to try and adapt them in this laboratory for use with tin cathodes.

Nickel.—Exner's conditions for nickel served very well for the determination of this metal (*Journ. Am. Chem. Soc.*, xxv., 899). There was no decided preference in the use of ammonium sulphate and ammonium hydroxide, or ammonium acetate and ammonium hydroxide as the electrolytes. The strong alkaline solutions should not stand longer than momentarily in the tin, unprotected by a current, but it is not necessary to have the circuit closed before putting in the reagents. The deposits were grey and very compact. A slight amount of loose material may be brushed out, and the dish used for another determination, but if too thick a coating of nickel is deposited it will be found very difficult to remove. The nickel was dissolved with potassium cyanide aided by the current or by nitric acid, specific gravity 1·52.

Faraday Society.—In consequence of the illness of Sir Oliver Lodge, the delivery of his Presidential Address arranged for Tuesday, March 24th, is postponed until further notice.

REVISIONS OF THE THEORY OF ELECTROLYSIS.*

By HENRY S. CARHART, LL.D

(Continued from p. 142).

From the time of Grotthus there was a long pause of fifty years in the theory of electrolysis, for no important step was taken until Clausius, in 1857, published his profound modification of the Grotthus theory. Clausius's study of the kinetic theory of heat prepared him to apply similar principles to the interpretation of electrolytic phenomena. He leaves no doubt about his meaning; his conceptions are always clear and clearly expressed. I will let him speak for himself (*Ann. der Physik*, 1857, ci.):—

"Let there be a liquid, consisting wholly or in part of electrolytic molecules; and let it be assumed that these molecules are arranged in the natural condition of the liquid in any definite manner in which they persist, so long as no foreign force acts on them, while the individual molecules oscillate perhaps about their positions of equal librium, but are unable to get quite away from them. Further, let an attraction be assumed between two part-molecules, as there must be in every possible arrangement, and let two part-molecules be bound together into a whole molecule and, therefore, very near together; then the attraction binding them together is greater than the attraction between the positive part-molecule of one complete molecule and the negative of another. If now an electric force acts within this mass, and seeks to urge the positively electrified part-molecules in one direction and the negatively electrified ones in the other, then the question arises what influence this electric force must exert on the behaviour of the molecules.

"Inasmuch as the molecules are assumed to be capable of rotation, the first effect would plainly be to turn all of them in the same manner, so that the two oppositely electrified portions of each complete molecule would be turned in the direction in which they are urged by the acting force. Further, the force would seek to separate the part-molecules united in a whole or complete one and to move them in opposite directions; and if this motion ensues, then the positive part molecule of one whole one would meet the negative of the following and would combine with it. But now, in order that the once united part-molecules may be separated, the attraction which they

* Presidential Address delivered at the Seventh General Meeting of the American Electro-chemical Society. From the *Smithsonian Report* for 1906, p. 147.

exercise on each other must be overcome. Therefore a force of definite strength is necessary, and one is thus led to the conclusion that so long as the force acting on the conductor does not have this strength no decomposition whatever can take place, and that, on the contrary, if the force is increased to the requisite strength very many molecules must be decomposed at the same time, since they are all under the influence of the same force and have precisely the same relation to one another.

"With respect to the electric current, the conclusion can be expressed as follows if it is assumed that the conductor conducts only through electrolysis: So long as the force acting on the conductor is below a certain limit it will produce no current whatever, but if it has reached this limit, then suddenly a very strong current will flow. But this conclusion is flatly contradicted by experience. Even the smallest force causes a current, conducted by alternate decompositions and reunions, and the intensity of this current increases in accordance with Ohm's law in proportion to the electromotive force.

"It follows from these considerations that the above supposition to the effect that the part-molecules of an electrolyte are bound together in the fixed relation of whole molecules, and that these have a definite and regular arrangement, must be untrue.

. . . .

"I believe, therefore, that the following hypothesis by which this contradiction is removed, and which, as it seems to me, is in harmony with other known facts, deserves some consideration.

"In my treatise 'On the Mode of Motion, which we call Heat,' I have expressed the view that in liquids the molecules have no definite positions of equilibrium, about which they only oscillate, but that their motions are so lively that they thereby constantly come into entirely changed and new relations to one another and move among one another in an irregular way.

"Let us now imagine in an electrolytic liquid a single part-molecule present, for example, an electro-positive one, the electrical condition of which we shall assume is exactly the same as at the moment when it was separated from a complete molecule. I believe now that while this part-molecule moves about among the whole molecules, under the many relations which it can assume, sometimes those will occur in which it will attract the negative part-molecule of an undissociated molecule with greater force than that with which the two parts belonging to an undissociated molecule, whose relation to each other is not entirely unchangeable, attract each other at this same instant. As soon as this condition occurs it will soon join itself to this negative part-molecule, and the positive part-molecule formerly bound to the same thereby becomes free. This one now in turn moves about free and after a time decomposes another whole molecule in the same manner, and so on. All these movements and decompositions occur in the same irregular manner as the heat motions by which they are set going.

. . . .

"When now in a liquid, whose molecules already find themselves in such motion that they exchange their part-molecules in an irregular way, an electric force acts which tries to drive all the positive part-molecules in one direction and the negative ones in the opposite, then it is easy to understand what differences in the mode of the molecular movements must ensue.

"A free part-molecule will then no longer follow the irregularly changing directions which it is forced to pursue by the heat motions, but it will change the direction of its motion to correspond with the acting force; so that although the motions of the positive part-molecules are very irregular still a certain direction will prevail among them; and likewise the negative part molecules will move under compulsion in the opposite direction.

. . . .

"If one considers within a liquid on which an electric force acts a small surface at right angles to the direction of the force, then through this area more positive part-molecules pass in unit time in the positive direction than in the negative, and more negative part-molecules in the negative than in the positive direction, . . . so that a certain excess number of positive part-molecules go in the positive direction and a certain excess number of negative part-molecules in the negative direction through the small area. The magnitude of these two numbers does not need to be the same, since it depends also, outside of the force urging them, which is the same for both, on the degree of their mobility, and this may for many reasons be different for different part-molecules.

"These opposite movements of the two kinds of part-molecules compose the voltaic current within a liquid.

. . . .

"By this conception of the state of liquids the difficulty mentioned above vanishes. It is readily seen that the influence which the electric force exerts on the irregular molecular decompositions and motions already existing does not begin when the force has reached a certain value, but that even the smallest force must act on them, and that the amount of this action must increase with the magnitude of the force. The entire process then agrees well with Ohm's law.

. . . .

"If we compare the older Grotthus theory with the one here developed, the difference lies chiefly in this: In the former it was assumed that the motion is first brought about by the electric force and takes place in two definite directions only, while the decompositions go on regularly from molecule to molecule, but in the latter the motions already present are only modified, not to the extent of making them entirely regular, but only so that among the great multitude of motions those in the two definite directions prevail."

These ideas of Clausius are so fundamental in the modern theory of electrolysis that I have thought it best to translate them freely rather than to paraphrase them. Clausius belongs to our own day. The grey hair and benign expression of this beautiful old man made a lasting impression on me as I saw him at the International Electrical Congress in Paris in 1881.

(To be continued).

Complete Analysis of Vegetable Matter.—J. M. Albahary.—The moisture and volatile matter in the fresh material are determined by drying at 110°. The ash is determined by carbonising the dry material, washing with boiling water, and igniting at a low temperature in a current of oxygen. The fresh material is triturated with alcohol and the residue gives the dry matter insoluble in alcohol. From the alcoholic liquid the volatile acids can be determined by titration with caustic soda. Colouring matter and fats are extracted with petroleum ether in a Soxhlet apparatus, using the dried extract of the plant. Reducing sugars, mineral acids, nitrogen, asparagine, and sulphur, &c., are estimated in the part which is insoluble in neutral alcohol.—*Comptes Rendus*, cxlvi., No. 7.

Simultaneous Production of 1.6 and 2.7-Dimethylanthracenes by the Action of CH_2Cl_2, $CHCl_3$, or of $C_2H_2Br_4$ on Toluene in Presence of $AlCl_3$.—James Lavaux.—When CH_2Cl_2 and $AlCl_3$ act on toluene the symmetrical ditolylmethanes para-para and meta-meta are first formed, $CH_3—C_6H_4—CH_2—C_6H_4—CH_3$. These under the action of CH_2Cl_2 yield dimethylanthracene dihydrides, which afterwards lose H_2, giving 2.7- and 1.6-dimethylanthracenes. $CHCl_3$ and $AlCl_3$ act similarly on toluene, the chief products of the reaction being the same dimethylanthracenes, and if it is assumed that dibromoditolylethanes are formed as intermediate products when $C_2H_2Br_4$ and $AlCl_3$ act on toluene, the formation of 1.6 and 2.7-dimethylanthracenes can readily be explained.—*Comptes Rendus*, cxlvi., No. 7.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 5th, 1908.

Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

Messrs. E. de B. Barnett, E. M. Eagles, R. C. Gale, J. M. Heron, C. W. Moore, A. R. Runeckles, H. E. Watson, and J. H. Williams were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Arthur Edward Coverdale, 68, Broad Street, Worcester; Frederick J. Maywald, 1028, 72nd Street, Brooklyn, N.Y., U.S.A.; Samuel Ernest Melling, The Cliff, Higher Broughton, Manchester; Edwin John Watkins, 10, Montpelier Road, Queen's Road, Peckham, S.E.

The President read the names of the Fellows recommended by the Council for election as Officers and as Ordinary Members of Council of the Society. It was also announced that the name of Prof. W. Jackson Pope, as Vice-President, and the names of Mr. John Allan and Prof. Adrian J. Brown, as Ordinary Members of Council, had been proposed by other Fellows.

Of the following papers, those marked * were read :—

*44. "*The Solubility of Iodine in Water.*" By Harold Hartley and Norman Phillips Campbell.

The solubility of iodine in water has been determined at 18°, 25°, 35°, 45°, and 55°, the value at 25° agreeing very closely with that found by Noyes and Seidensticker. The heat of solution has been calculated from the temperature coefficient of the solubility.

*45. "*Nitro-derivatives of o-Xylene.*" (Preliminary Note). By Arthur William Crossley and Nora Renouf.

o-Xylene, when treated with a nitrating mixture, readily yields two trinitro-derivatives, which can be separated by means of their different solubilities in concentrated sulphuric acid. Both crystallise from alcohol, in which solvent they are fairly readily soluble, the one in faintly yellow glistening flattened needles, melting at 71°, and the other in long stout prismatic needles, melting at 115°.

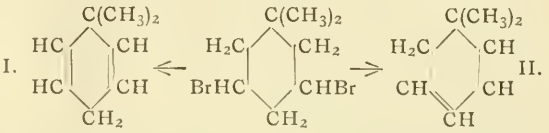
These facts are not in accord with the statement of Noelting and Thesmar (*Ber.*, 1902, xxxv., 634), that "*o*-xylene is incapable of yielding a trinitro-derivative even when submitted to the action of the strongest nitrating agents." The explanation of this statement is probably as follows :—Noelting and Thesmar further nitrated 4-nitro-*o*-xylene, melting at 29—30°, and obtained two dinitro-xylenes, melting respectively at 115—116° and 75—76°. The present authors arrived at the same results on repeating these experiments, except that they have not, so far, been able to raise the melting-point of the latter substance above 71°. There are therefore a dinitro- and a trinitro-*o*-xylene, melting at 71°, and also a dinitro- and a trinitro-*o*-xylene melting at 115°. When Noelting and Thesmar submitted 4-nitro-*o*-xylene to the action of a nitrating mixture above a temperature of 100°, they doubtless obtained the two trinitro-derivatives melting at the same temperatures as their dinitro-compounds. The mixed melting-point method, however, shows the substances to be quite distinct; the dinitro- and trinitro-derivatives, melting at 71°, when mixed in equal quantity, melt at 45—50°, becoming quite clear at 63°; and the dinitro- and trinitro-derivatives, melting at 115°, when mixed, melt at 82—83°, and become quite clear at 86°.

During the course of these experiments, a third dinitro-*o*-xylene, melting at 82°, has been isolated, and another substance, melting at 115°, which is not a nitroxylene, but a nitro-derivative of some condensed benzene ring derivative.

The authors are continuing the experiments, more particularly in the direction of the orientation of these hitherto unknown-*o*-xylenes.

*46. "*Substituted Dihydrobenzenes.* Part II. 1 : 1-*Dimethyl*-Δ^2 : 4-*dihydrobenzene and* 1 : 1-*Dimethyl*-Δ^2 : 5-*dihydrobenzene.*" By Arthur William Crossley and Nora Renouf.

Dimethyldihydrobenzene has been prepared by the elimination of two molecules of hydrogen bromide from 3 : 5-dibromo-1 : 1-dimethylhexahydrobenzene, and the resulting hydrocarbon has been proved to consist of a mixture, in approximately equal parts, of 1 : 1-dimethyl-Δ^2 : 4-dihydrobenzene (II.) and 1 : 1-dimethyl-Δ^2 : 5-dihydrobenzene (I.). A detailed study of the properties of these substances leads to the conclusion that the 1 : 1-dimethyl-Δ^2 : 4-dihydrobenzene described by Crossley and Le Sueur (*Trans.*, 1902, lxxxi., 821) has the constitution ascribed to it, despite the adverse criticisms of Harries and Antoni (*Annalen*, 1903, cccxxviii., 88); but it contains traces of some oxygenated substance, probably a methoxy-derivative.



47. "*The Viscosity of Aqueous Pyridine Solutions.*" By Albert Ernest Dunstan and Ferdinand Bernard Theodore Thole.

In view of the criticism to which their former work (*Trans.*, 1907, xci., 1718) has been subjected (*Proc.*, 1908, xxiv., 22), the authors have repeated their experiments on the viscosity of aqueous pyridine solutions, and find that the same discontinuities occur in the curve as were previously observed.

Discussion.

Mr. Hartley said that he understood Mr. Dunstan to use the word "discontinuity" to denote a point where two supposed sections of a curve pass imperceptibly into one another, but, as under these conditions the curve is continuous, he thought the use of the term "discontinuity" was very misleading. The only evidence for the existence of the secondary irregularities which Messrs. Dunstan and Thole had endeavoured to prove depended on discontinuities in lines drawn through series of experimental points without making any allowance for experimental error. Such a method of argument was only allowable if around each point a circle was described of radius equal to the probable experimental error. If this were done in the case of the physical properties of mixtures of pyridine and water, he thought that a smooth curve could be drawn through the series of circles so obtained, as had been found by Thomas, Appleby, and himself.

Mr. Dunstan agreed with Mr. Hartley as to the difficulty of expressing the change of curvature in a simple way, and thought that perhaps the term "discontinuity" was the simplest in the light of his explanation of the curves. With reference to Mr. Hartley's system of plotting, he was quite in agreement with it, having, as a matter of fact, taken similar precaution in allowing for experimental error.

*48. "*The Action of Thionyl Chloride on the Methylene Ethers of Catechol Derivatives.* II. *Piperonyloin, Piperil, and Hydropiperoin.*" By George Barger and Arthur James Ewins.

By heating the methylene ethers, mentioned in the title, with thionyl chloride to 180—200°, cyclic *dicarbonates* result, which in all cases contain chlorine. By elimination of chlorine from the substance derived from piperonyloin and from piperil, the *dicarbonate* of *tetrahydroxybenzil* and *tetrahydroxybenzil*, $(OH)_2C_6H_3{\cdot}CO{\cdot}CO{\cdot}C_6H_3(OH)_2$, m. p. 237°, was obtained.

A number of other derivatives were described.

49. "*Traces of a New Tin-group Element in Thorianite.*" By Clare de Brereton Evans.

In the course of an examination of some residues of 5 cwt. of thorianite belonging to Sir William Ramsay, traces of a supposed new element were discovered associated with the sulphides of the tin-group.

The dark brown sulphide was separated with arsenious sulphide, which it resembles in being insoluble in hydrochloric acid, and readily soluble in ammonium carbonate solution, to which it gives a characteristic deep brown colour. In addition to these reactions, it dissolves readily in water, forming a deep brown solution; it is scarcely attacked by a mixture of hydrochloric acid and potassium chlorate, but dissolves in nitric acid, forming, on evaporation at 100°, a golden-red syrup, which leaves behind a hygroscopic brown oxide at 120—130°. A grey metal was obtained by reduction in hydrogen, but the quantity was too small to allow of its equivalent being determined.

Incidentally, proof was obtained of the presence in thorianite of arsenic, mercury, bismuth, molybdenum, and selenium, in addition to those elements already discovered in the mineral.

A new triple oxalate of thorium, uranium, and ammonium was described; it appears to have the composition $ThU_{25}(NH_4)_2(C_2O_4)_{10},14H_2O$.

50. "*The Sulphination of Phenolic Ethers and the Influence of Substituents.*" By Samuel Smiles and Robert Le Rossignol.

The authors have previously drawn the conclusion (*Proc.*, 1906, xxii., 158; *Trans.*, 1906, lxxxix., 696) that the sulphonium base derived from phenetole is produced in three stages at which the sulphinic acid, sulphoxide, and base are consecutively formed. The sulphinic acid, however, had not been observed in the products of the reaction, and thus the evidence was incomplete. The above view of the mechanism of the reaction has now been confirmed by the isolation of the sulphinic acid from substituted phenolic ethers. It is proposed to apply to the entire process the name "sulphination." The behaviour of benzene, toluene, and homologous phenolic ethers has been investigated, and it was shown that the products vary according to the position of the methoxyl and methyl groups. Generally speaking, the presence of a group in the ortho-position with respect to the entrant quadrivalent sulphur atom tends to prevent the formation of sulphonium base; on the other hand, this is favoured by groups of strong directing influence.

51. "*The Relation between Unsaturation and Optical Activity.* Part II. *Alkaloid Salts of corresponding Saturated or Unsaturated Acids.*" By Thomas Percy Hilditch.

The study of the relative effects of saturated and unsaturated acids on an optically active base has been extended to alkaloid salts of β-phenylpropionic, cinnamic, phenylpropiolic, and succinic, maleic, fumaric, and acetylenedicarboxylic acids. Salts of brucine, coniine, codeine, and cinchonine have thus been examined polarimetrically in chloroform solution, and the results show very clearly that the change in optical rotatory power is influenced not only by the simple change of constitution associated with increasing unsaturation, but also by the structure of the base and the type of acid used. Thus, in general, the effect observed in the case of coniine salts differs from those observed with the derivatives of more complex bases, and appears to be of the same kind as that observed by Walden with the active amyl esters of the same series of acids. It is noticeable, however, that in all the instances now brought forward the change to an ethylenic linking is accompanied by an increase in optical effect.

52. "*The Wandering of Bromine in the Transformation of Nitroaminobromobenzenes.*" By Kennedy Joseph Previté Orton and Constance Pearson.

2 : 6-Dibromo-1-nitroaminobenzene, when dissolved in aqueous, aqueous alcoholic, or acetic acid solutions of hydrochloric or sulphuric acids, yields not only 2 : 6-dibromo-4-nitroaniline, but also the isomeric 2 : 4-dibromo-6-nitroaniline, the nitro-group having partly migrated to the vacant para-position, and having partly displaced an atom of bromine from one of the ortho-positions.

The use of hydrobromic or nitric acid in the same solvents leads largely to the reduction of the nitroamine to the diazo-compound, but at the same time migration of the nitro-group and displacement of bromine occur.

In a comparison, the behaviour of other nitroamines when similarly treated was described.

53. "*A New Isomeride of Vanillin occurring in the Root of a Species of* Chlorocodon." (Preliminary Note). By Ernest Goulding and Russell George Pelly.

A sample of the root of a species of *Chlorocodon* (probably *C. Whiteii*) was forwarded for examination to the Imperial Institute from Uganda, where the plant is known by the native name of "Murundo." This root has a pleasant odour, intermediate between those of vanillin and piperonal, and is said to be chewed by the natives for sweetening the breath.

The powdered root, on distillation with steam, yields 0·5 per cent of a crystalline *substance*, $C_7H_5O_2{\cdot}OMe$, which separates from the distillate in thin lustrous colourless plates, having the characteristic odour of the root. It melts at 41—42° and boils at 257—258°, a pale brown coloration being developed. The substance is readily soluble in most organic solvents, and fairly so in hot, but only sparingly so in cold, water. An aqueous solution gives a red or purplish brown coloration with ferric chloride, and, on warming a solution with ammoniacal silver nitrate, the latter undergoes reduction with the separation of silver. It dissolves freely in dilute alkali hydroxide, and is re-precipitated by acids. The aqueous solution does not give a precipitate with lead acetate.

The *oxime*, $OMe{\cdot}C_6H_3(OH){\cdot}CH{:}N{\cdot}OH$, crystallises in large, thin, lustrous, transparent plates melting at 138°; it is almost odourless, and readily soluble in hot water but sparingly so in cold.

The *phenylhydrazone*, $OMe{\cdot}C_6H_3(OH){\cdot}CH{:}N{\cdot}NHPh$, crystallises from hot alcohol in pale yellow lustrous plates, and melts at 137—138°.

The *sodium* derivative, $OMe{\cdot}C_6H_3(CHO){\cdot}ONa$, obtained by the addition of alcoholic sodium hydroxide to an alcoholic solution of the substance, separates in small, almost colourless, lustrous plates, and dissolves readily in water to form a pale yellow solution which is strongly alkaline.

These results, together with the analytical data obtained, show that the odorous constituent of *Chlorocodon* root is a monomethyl ether of a dihydroxybenzaldehyde, $OMe{\cdot}C_6H_3(OH){\cdot}CHO$, which is not identical with vanillin or any of its known isomerides.

Unfortunately, the amount of material available was so small that it has not been possible to carry out experiments with the object of ascertaining the relative positions of the hydroxy-, methoxy-, and aldehyde-groups, but the authors intend to continue the work in this direction as soon as a further supply of the root has been obtained.

54. "*The Volatile Oil of the Leaves of* Ocimum viride." (Preliminary Note). By Ernest Goulding and Russell George Pelly.

A consignment of the leaves of *Ocimum viride*, forwarded for examination to the Imperial Institute from Sierra Leone, has been examined with the following results:—On distillation with steam, the leaves yielded about 0·35 per cent of an orange-yellow, volatile oil, which is very mobile, has an aromatic, thyme-like odour, a spicy pungent taste, D 15/15 0·9115, $[\alpha]_D$ +1° 30′ (approx.), and is soluble in all proportions in 90 per cent alcohol.

When distilled under the ordinary pressure 100 cc. of the oil yielded 25 cc. boiling at 165—180° with D 15/15 0·8614 and $[\alpha]_D$ +0° 33′; 20 cc. at 180—200°, with D 15/15 0·8804 and $[\alpha]_D$ +1° 40′; 20 cc. at 200—220°, with D 15/15 0·9164 and $[\alpha]_D$ +2° 38′; 20 cc. at 220—235°, with D 15/15

0·9548 and $[\alpha]_D +3^\circ 38'$; and 10 cc. at 235—250°, with D 15/15 0·9565 and $[\alpha]_D +5^\circ 14'$.

The composition of the oil is approximately as follows: Thymol, 32 per cent; alcohols (calculated as $C_{10}H_{18}O$), 40 per cent; esters (calculated as $C_{10}H_{17}\cdot OAc$), 2 per cent; the remainder consists chiefly of a terpene (or possibly a mixture of terpenes), $C_{10}H_{16}$, which is a mobile, highly refractive liquid of pleasant lemon-like odour, boiling at 160—166°, and having D 15/15 0·8456 and $[\alpha]_D +0^\circ 10'$.

The authors intend to make a more complete examination of the oil as soon as a larger supply of material has been received.

55. "*Experiments on the Synthesis of the Terpenes.* Part XII. *Synthesis of Terpins, Terpineols, and Terpenes derived from the Methylisopropylcyclopentanes*, $Me\cdot C_5H_8\cdot CHMe_2$." By Walter Norman Haworth and William Henry Perkin, jun.

An account was given of the synthesis of terpenes, such as $CH\begin{matrix}CH\cdot CH_2\\ CHMe\end{matrix}>CH\cdot CMe:CH_2$, which are analogously constituted to dipentene, but contain a *cyclo*pentene in the place of the *cyclo*hexene ring of the latter. The corresponding five-ring terpineols and terpins were also described.

56. "*The Initial Change of the Radium Emanation.*" By Nevil Vincent Sidgwick and Henry Thomas Tizard.

In their paper on this subject, Cameron and Ramsay (*Trans.*, 1907, xci., 1266) have shown that, after the removal of the hydrogen and oxygen, the radium emanation diminishes rapidly (in about an hour and a-half) to one-half of its initial volume. Hence it follows that the emanation (or a constituent) polymerises; the possibility of the simultaneous formation of helium or of a solid they consider they have disproved.

By measuring the rate of change, they show that the reaction is unimolecular; that is, the rate is proportional only to the amount of changing substance. They assume that two molecules of the original emanation Em_I polymerise to one molecule of Em_2, and they say (p. 1280) "this involves an exponential curve, and that has been realised." But their exponential curve implies a unimolecular reaction, and a polymerisation cannot in the nature of things be unimolecular, since it necessarily involves the combination of two or more molecules. The reaction—

$$2Em_I = Em_2$$

must be bimolecular, and, in general, any polymerisation must be a reaction of the n^{th} order, where n is the number of molecules that combine.

Hence the change they are measuring cannot be the polymerisation, and, as it is unimolecular, must be of the form—

$$Em_I = Em',$$

and the polymerisation which obviously occurs must follow this change, and must be rapid. We therefore have:—

1. $Em_I = Em'$ (Slow: unimolecular)
2. $nEm' = Em_2$ (Quick: n-molecular)

Cameron and Ramsay assume that $n=2$; that two molecules of Em_I give one of the final product. But this is not a necessary result of their equation, for, if the first reaction is unimolecular, we get—

$$-\frac{dV'_t}{dt} = kV'_t;$$

where V'_t is the amount of the changing substance Em_I (or its volume reduced to standard pressure) at the time t from the true beginning of the reaction, the observed volume of gas being V_t. Now if n molecules of the first product (Em') polymerise to one molecule of Em_2, the amount of Em_2 present at time t is obviously—

$$(V_o - V_t)\frac{1}{n-1};$$

where V_o is the total volume of gas at the beginning.

Therefore—

$$V'_t = V_t - (V_o - V_t)\frac{1}{n-1}$$
$$= \frac{nV_t - V_o}{n-1}$$
$$= \frac{n(V_t - V_\infty)}{n-1},$$

since V_∞, the final volume, $= V_o/n$.

Hence—

$$-\frac{dV'_t}{dt} = \frac{n}{n-1}\cdot\frac{dV_t}{dt} = kV'$$
$$= \frac{n}{n-1}\cdot k\cdot(V_t - V_\infty).$$

Therefore—

$$-\frac{dV_t}{dt} = k\cdot(V_t - V_\infty).$$

Integrating this, under the condition that when $t=0$ $V_t = V_o$, we obtain—

$$\log\frac{V_o - V_\infty}{V_t - V_\infty} = kt,$$

which is the expression that Cameron and Ramsay have shown to agree with the experimental results. It is obvious that it is equally compatible with any value of n.

Their reason for assuming that $n=2$ is that during the time of observation the volume of the gas diminishes to about a half; and they suppose that the time when the first observation is made is the actual beginning of the change, and that the gas then wholly consists of Em_I. It is, however, difficult to see how the reaction cannot have begun earlier than this. The emanation gradually accumulates in and over the solution of the radium salt for several days; it is then transferred to the explosion-burette, exploded, the emanation and the residual hydrogen passed over phosphoric oxide and cooled with liquid air, the hydrogen pumped off, and the emanation allowed to evaporate and passed into the capillary. Mr. Cameron informs us that the time taken in the purification is less than an hour, and the time elapsing between the evaporation of the emanation and the first measurement is less than a quarter of an hour. It seems scarcely possible that the change of Em_I to Em', which, as it is unimolecular, is not affected by the dilution, should not take place during these operations, and yet when they are finished should begin with a velocity which takes it to half completion in about nine minutes. A more probable hypothesis is that the change has already proceeded some way before the observations begin, and that the actual number of molecules of Em_I which go to form one molecule of Em_2 is greater than 2. Even if the reaction only begins when the liquid air has been removed, and the gas has assumed the temperature of the room, something like half the initial volume of Em_I must have changed before the first measurement is made. On the other hand, the change cannot have continued during the whole time that the emanation has been accumulating, for, if we reckon the time backwards, the volume must increase a thousand-fold every ninety minutes. It would therefore appear that for some reason the reaction does not begin until the liquid air is removed; before this point, the Em_I must have been in a different chemical state. But as soon as the emanation has evaporated, it must begin to change at once, and, as it is not measured for nearly ten minutes after this, the volume of Em_I at the first measurement cannot be much more than half the true initial volume, the period of half decay being about nine minutes. Hence the final volume is at most one-third of the initial, and n cannot be less than 3.

PHYSICAL SOCIETY.

Ordinary Meeting, March 13th, 1908.

Dr. CHARLES CHREE, F.R.S., President, in the Chair.

THE following candidates were elected Fellows of the Society:—Mr. A. E. Garratt, Mr. A. E. Hall, and Mr. W. Williams.

A paper on "*The Distribution in Electric Fields of the Active Deposits of Radium, Thorium, and Actinium*" was read by Mr. S. RUSS.

The first experiments were made with the active deposit produced from radium emanation. Whereas the amount of active deposit directed to a cathode decreases as the pressure in the containing vessel is reduced, after a certain pressure is reached, it was found that the amount going to an anode shows a corresponding increase under the same conditions. A comparison was made over a range of pressure extending from 0·01 mm. to 1·2 mm., between the amounts of active deposit obtained on a rod made positive or negative when exposed to the same quantity of radium emanation for equal periods of time. The main feature brought out by this comparison is that at the lowest pressure reached almost as much activity is obtained on the anode as on the cathode, while at atmospheric pressure the activity of the latter is about twenty times that of the former. Similar experiments conducted in hydrogen, air, and sulphur dioxide, three gases differing considerably in density, indicate that the collisions between the active deposit particles and the gaseous molecules play an important part in the ultimate distribution of the active deposit in electric fields. Experiments on similar lines with thorium and actinium show that while at atmospheric pressure nearly the whole of the active deposit particles of thorium are directed to the cathode, this is not necessarily the case with actinium, for it was found that under certain conditions the activity of the anode was fully one-half that of the cathode. Some observations made more recently than those cited above indicate that the sign of the electrical charge exhibited by the active deposit particles of actinium is a function of the distance that these particles have travelled through the containing gas before reaching the electrodes.

Dr. C. H. LEES expressed his interest in the paper, referring especially to the fact that the amount of active deposit which diffused on to a neutral rod varied with the pressure.

The CHAIRMAN referred to the radio-activity of the atmosphere, and remarked that the author's experiments might be of use to meteorologists in enabling them to settle the question of the source of the radio-activity. He expressed his interest in the results obtained with actinium.

Mr. RUSS, in reply to Dr. Lees, said that the fact that the quantity of active deposit on a neutral rod varied with the pressure was being investigated mathematically by Mr. Bateman. With regard to the Chairman's remarks he observed that the source of the radio-activity of the atmosphere was an interesting question. The radio-activity due to thorium presented more difficulties than that due to radium because of the long life of the radium emanation. He suggested that the results might be due to the active deposits themselves which had longer lives than the emanations.

A "*Note on certain Dynamical Analogues of Temperature Equilibrium*," by Prof. G. H. BRYAN, was read by the Secretary.

The note calls attention to the following results of a method described by the author in 1900 (*Archives Néerlandaises*) under the title of "Energy Accelerations":—1. In a system of uniformly distributed particles, a stationary state of statistical equilibrium cannot exist under the Newtonian law of force whether the forces between the particles be attractive or repulsive except when the particles are at rest in a state of unstable equilibrium. 2. For energy-equilibrium to exist the force between the particles, if repulsive, must vary according to a higher power of the inverse distance than the square (*e.g.*, the inverse fifth power); if attractive it must vary according to a lower inverse power than the square of the distance. 3. In a system in which the kinetic energy cannot be expressed as a quadratic function of the velocities with constant coefficients, the equations of energy-equilibrium no longer take the form of linear relations between the various components of kinetic energy, so that the commonly assumed analogue between temperature and kinetic energy becomes inapplicable.

Prof. CASSIE discussed the method and results of the paper, and remarked that the results of experiments appeared to indicate that the forces between particles varied with the distance according to some law more rapid than the inverse fifth power.

A paper on '*Experiments on Artificial Fulgurites*" was postponed.

NOTICES OF BOOKS.

Immune Sera. By Dr. CHARLES FREDERICK BOLDUAN. Second Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1907.

THIS small book contains a good introduction to the study of immunity and immune sera. It is based upon a monograph by Prof. Wassermann, which was translated into English by the author, who has added in this edition chapters on snake venoms and their antisera, agglutinins, opsonins, &c., and has also discussed some aspects of the subject rather more fully than was possible in Prof. Wassermann's small book. The development of our knowledge of each group of immune sera is traced in short historical accounts, which are distinguished by unbiassed judgment and clearness of expression. A chapter on serum sickness gives a brief description of the clinical manifestations which sometimes follow the injection of diphtheria antitoxic serum, and of the means which may be taken to allay them.

MEETINGS FOR THE WEEK.

MONDAY, 30th.—Royal Society of Arts, 8. (Cantor Lecture). "Fuel and its Future," by Prof V. B. Lewes.

TUESDAY, 31st.—Royal Institution, 3. "The Egyptian Sudan—its History, Monuments, and Peoples, Past and Present," by E. A. Wallis Budge, M.A., &c.

—— Royal Society of Arts, 8. "Enamel Portraits," by Cyril Davenport.

WEDNESDAY, April 1st.—Royal Society of Arts, 8. "Dr. Schlick's Gyroscopic Apparatus for Preventing Ships from Rolling," by M. Wurl.

—— Society of Public Analysts, 8. "Lead in Tartaric Acid, Cream of Tartar, and Baking Powders," by The President. "The Nitrogen Factor for Casein" and "The Recovery of Amyl Alcohol from Waste Gerber Liquors," by H. D. Richmond. "Carapa Oil," by J. Lewkowitsch. "Rapid Method for the Estimation of Mercuric Salts in Aqueous Solution," by S. G. Liversedge.

THURSDAY, 2nd.—Royal Society of Arts, 8. (Howard Lecture). "The Navigation of the Air," by H. S. Hele-Shaw, F.R.S., &c.

—— Royal Institution, 3. "The Animals of Africa," by R. Lydekker, F.R.S.

—— Chemical, 8.30. "Condensation of Epichlorhydrine with Phenols," by D. R. Boyd and E. R. Marle. "Rate of Hydrolysis of Chloroacetates and Bromoacetates and of α-Chlorhydrine by Water and by Alkali, and the Influence of Neutral Salts on the Reaction Velocities," by G. Senter. "New General Method of Preparing Diazonium Bromides," by F. D. Chattaway. "Probable Nature of the Impurity found in the Triphenylmethane Spectrum," by W. N. Hartley. "Absorption Spectrum of Triphenylmethane," by A. G. G. Leonard. "Constituents of Cyprus Origanum Oil—Isolation of a New Terpene (Origanene)," by S. S. Pickles.

FRIDAY, 3rd.—Royal Institution, 9. "The Modern Motor Car," by the Right Hon. Lord Montagu of Beaulieu

SATURDAY, 4th.—Royal Institution, 3. "Electric Discharges through Gases," by Prof. J. J. Thomson, F.R.S.

THE CHEMICAL NEWS.

Vol. XCVII., No. 2523.

LUTECIUM AND NEO-YTTERBIUM.

By G. URBAIN.

In a note which I presented to the Académie on November 4th, 1907, I showed that Marignac's ytterbium was a mixture of two elements, which I defined by their spectral properties and the approximate values of their atomic weights. The element with atomic weight about 174 I called lutecium, and I gave the name neo-ytterbium to the element with lower atomic weight. By keeping the term ytterbium in this last name I left the honour of his original discovery to Marignac.

In this note I propose to give some details, which, although important, could not be included in the first summary of my experiments.

These researches on ytterbium extend back to 1904 when I began to examine the earths from xenotime, from which I had first extracted the ytterbia. The first experiments eliminated the earths of the cerium group, gadolinium, terbium, dysprosium, and holmium. This was effected by the fractional crystallisation of the ethyl sulphates. The last mother-liquors contain only yttrium, erbium, thulium, and the ytterbiums. The greater part of the yttrium was eliminated by the fractional ignition of the nitrates. The nitrates of the earths of high atomic weight are more easily decomposed than yttrium nitrate in nitric acid of density 1·3. These earths were then fractionated by the crystallisation of the nitrates with five molecules of water. By this method in some months the greater part of the raw ytterbium which is concentrated in the mother-liquor could be separated. The raw ytterbia was then fractionated by the same method, and divided into 22 consecutive fractions. No fewer than 15,000 successive crystallisations were necessary to get these results. This extremely tedious work was completed by a series of spectral measurements and of atomic weight determinations, of which only the most important results can be given.

The following are the numbers obtained for the atomic weight by transforming the octohydrated sulphates into oxides by heat. The international atomic weights were adopted, O = 16.

No. of fraction.	Weight of octohydrated sulphate.	Weight of oxide.	Atomic weight.
17.	1·3650	0·6859	170·66
18.	1·6545	0·8352	171·89
19.	1·7255	0·8722	172·42
20.	2·1674	1·0970	172·94
21.	2·8650	1·4500	172·91
22.	2·2545	1·1412	172·98
23.	2·4411	1·2363	173·18
24.	3·2193	1·6315	173·45
25.	3·2743	1·6597	173·53
28.	3·1227	1·5842	173·89
29.	3·1565	1·6015	173·91
30.	2·4756	1·2565	174·04
30.	3·1267	1·5868	174·02

By the fractional precipitation with dilute soda of a solution of ytterbium sulphate of mean atomic weight 173·5, I obtained the following numbers for the extreme fractions :—

	Octohydrated sulphate.	Oxide.	Atomic weight.
First fractions (weakest bases)..	3·6358	1·8443	173·82
Last fractions (strongest bases) .	3·2868	1·6584	171·70

The fractionation extended to 16 consecutive fractions; the total number of precipitations was 240. From this it is seen that lutecium is a weaker base than neo-ytterbium. I observed the same spectral differences between the extreme members of this fractionation as between the extreme members of the fractionation of the nitrates.

G. Jantsch and I, when we determined the magnetic susceptibility of these oxides, found considerable differences. The two earths appear paramagnetic; neo-ytterbium is much more magnetic than lutecium. The susceptibility of my best earths is in the ratio 53 : 13.

At the meeting on December 19, 1907, *i.e.*, forty-four days after my report to the Paris Académic des Sciences, Auer von Welsbach, without alluding to my researches, communicated a short note to the Vienna Académie des Sciences, in which he agreed with me in regarding ytterbium as a mixture of two elements. He characterised them only by the atomic weights 174·5 and 172·9, and merely stated that there are differences in their spectra, without further defining them.

He called the first aldebaranium and the second cassiopeïum. Aldebaranium is evidently identical with lutecium and cassiopeïum with neo-ytterbium.

It is true that Auer von Welsbach and I, independently of one another, have studied the same question for some years, as I have already stated in my first note: it is not less true that I was the first to give numerical results, both of atomic weight determinations and of spectral measurements, to characterise the new elements. As Auer von Welsbach's communication only confirms researches previously published there can be no question of new names for lutecium and neo-ytterbium, which have already been named.—*Comptes Rendus*, vol. cxlvi., No. 8, p. 406.

THE FLUORIDES OF GADOLINIUM, NEODYMIUM, AND PRASEODYMIUM.

By J. POPOVICI.

The salts of gadolinium have been investigated and described by C. Benedicks (*Zeit. f. Anorg. Chem.*, 1900, xxii., 393). Gadolinium fluoride, which has not yet been described, I have obtained by precipitating a concentrated gadolinium sulphate solution with hydrofluoric acid. The nitrate, which was used as the initial material, was first converted into the difficultly soluble sulphate, which crystallises very readily. A concentrated aqueous solution of the sulphate gives a colourless gelatinous precipitate with hydrofluoric acid. When this precipitate is warmed on a water-bath a white granular powder settles. This is filtered off and washed with cold water; the fluoride is rather soluble in hot hydrofluoric acid, insoluble in water.

The substance was analysed by evaporating it with concentrated sulphuric acid, and thus converting it into the corresponding sulphate, which yields the oxide (Gd_2O_3) when it is strongly heated with small quantities of ammonium nitrate. Its orange-yellow colour is probably caused by traces of terbium oxide, as Benedicks has shown (*Ibid.*). Acids have hardly any effect on the oxide in the cold, but dissolve it completely on warming.

0·1659 grm. substance : 0·1396 grm. oxide. GdF_3 : Calculated, Gd 73·23; found, Gd 72·94

The fluorides of neodymium and praseodymium have been mentioned by H. Moissan (*Comptes Rendus*, 1900, cxxxi., 595) as the products of the ignition of the corresponding carbides in fluorine gas. When hydrofluoric acid is added to solutions of the nitrates the fluorides result as gelatinous precipitates.

The neodymium precipitate is deposited on warming as a pale lilac-coloured crystalline powder. The praseodymium precipitate, when filtered off, dried in the air and in a desiccator, gives yellowish glittering crystals which appear green by reflection. Both fluorides were converted into sulphates and oxides. Neodymium fluoride, on ignition with small quantities of ammonium nitrate, gave the white higher oxide corresponding to the formula Nd_2O_5. According to Bohuslav Brauner's statements (*Chem. Soc. Proc.*, 1897—8, 70; *Chem. Zentralbl.*, 1898, I., 919) the oxide obtained by him contained rather more

oxygen than corresponds to the formula Nd_2O_5. He suggested that the element could probably be further split up, and would yield the oxide, Nd_2O_6.

Praseodymium contains traces of samarium, and thus rather high values have been obtained. But since the halogen compounds of neodymium and praseodymium have the same composition, praseodymium fluoride has probably the same formula as neodymium fluoride, NdF_3. Calculated, Nd 71·58; found, Nd 71·34.—*Berichte*, 1908, xli., 634.

NOTE ON THE PURIFICATION OF MERCURY.

By WILLIAM BETTEL.

Some twelve years ago, while engaged upon the examination of a "refractory" gold ore, I used weighed quantities of mercury (containing about 16 mgrms. gold per kilo., this being the purest mercury purchasable in Johannesburg at that time) together with a weak solution of cyanide, for combined amalgamation and cyanide treatment (in imitation of crushing with weak cyanide solution and amalgamation). My first experiment not yielding very encouraging results, the duplicate experiment was set aside for about a week. At the end of that period I collected the mercury, and found that it was free from gold, the whole of the "free" gold in the ore, together with that originally present in the mercury, having been dissolved by the cyanide solution. Cyanide, as is well known, has been in use for many years in amalgamation for keeping the "plates" in good condition, but its use in this connection has been deprecated owing to the likelihood of loss of gold through the solvent action of the cyanide on the fine ("float") gold; but, to me, it was a novelty to know that gold (amalgam) in solution in mercury could be so readily removed.

Until recently I regarded this reaction as merely an interesting chemical novelty, but having to purify about 7 kilos. of impure mercury (containing zinc, tin, lead, copper, iron, and gold, 150 mgrms. per kilo.) I decided, before resorting to distillation, to subject the mercury to a treatment with cyanide, using sodium peroxide to shorten the operation by facilitating oxidation of the "base" metals.

The metal was placed in a shallow enamelled iron pan with flat bottom, the mercury thus exposing its maximum area to the cyanide solution. The latter consisted of 1500 cc. of a 2·0 per cent solution of "98" per cent cyanide, together with 20 grms. of Na_2O_2 added at intervals. This solution was allowed to act upon the mercury, the whole being gently agitated at intervals.

For the first four days of treatment, during which the "base" metals were being dissolved, only traces of gold were dissolved, but on the fifth day the gold contents dropped from 150 to 90 mgrms. per kilo. The bulk of the base metals being removed, the gold now dissolved rapidly, as will be seen from the following record:—

Gold Contents.

Sixth day of treatment..	..	12	mgrms.	per	kilo. of Hg.
Seventh "	.. ..	6	"	"	"
Eighth "	.. ..	5	"	"	"

The solution was now removed, and replaced by one of one-tenth its strength. On the fourteenth day of treatment the gold contents of the mercury were too minute to be estimated, being under 1/50 mgrm. fine gold per kilo.

The mercury after this treatment is purer than that usually obtained by distillation *in vacuo*. The mercury dissolved by the cyanide solution is quite negligible in amount, so that the cost of purification is practically that of the cyanide used.

This process of mercury refining may therefore be made use of in chemical laboratories, &c., in preference to the distillation method.

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Johannesburg, Transvaal, South Africa.

THE ACTION OF THIONYL AND SULPHURYL CHLORIDES ON SELENIUM AND SELENIUM DIOXIDE.

By VICTOR LENHER and H. B. NORTH.

When selenium dioxide and thionyl chloride are brought together the two begin to react immediately, considerable heat is liberated, and the needle-like crystals of the dioxide are quickly changed to a white and finely divided crystalline powder. When the reaction is carried out in a sealed tube and heat applied, larger crystals can be obtained. Examination of these crystals showed them to be selenium tetrachloride, the reaction being as follows:— $2SOCl_2 + SeO_2 = SeCl_4 + 2SO_2$.

When the tubes are opened the sulphur dioxide escapes, and the excess of thionyl chloride can be removed from the crystals of the selenium tetrachloride by extraction with carbon bisulphide.

A more satisfactory method of carrying out this reaction consists in placing the selenium dioxide in a porcelain boat in a glass tube and heating in the vapour of thionyl chloride.

Selenium tetrachloride prepared in this manner gave on analysis—

	I.	II.	Calculated for $SeCl_4$.
Se.. ..	35·76	36·05	35·83
Cl.. ..	64·01	64·10	64·17

Selenium and Thionyl Chloride.—When selenium is brought in contact with thionyl chloride at the ordinary temperature only very slight action takes place, but when the two are sealed together in a tube and heated they react on each other more readily as the temperature is raised. In two weeks' time, by continuous heating at 200°, a few grms. of selenium tetrachloride can be produced, while at 300° the same quantity of substance can be formed in a few hours. In carrying out this experiment it is more convenient, both for readiness in carrying out the reaction and for obtaining a purer product, to heat the elementary selenium in a porcelain boat in a glass tube in the vapour of thionyl chloride. The reaction takes place as follows:— $2SOCl_2 + Se = SeCl_4 + SO_2 + S$.

Analysis of the product formed gave—

	I.	II.	Calculated for $SeCl_4$.
Se.. ..	35·63	35·66	35·83
Cl.. ..	64·51	64·31	64·17

Selenium and Sulphuryl Chloride.—When these two substances are brought together, reaction immediately ensues, a large amount of heat is liberated, and on cooling selenium tetrachloride deposits in crystals. This reaction, like the previously described ones, can be advantageously carried out by heating the selenium in the vapour of sulphuryl chloride. The reaction takes place as follows: —$2SO_2Cl_2 + Se = SeCl_4 + 2SO_2$.

Analysis of the tetrachloride showed—

	I.	II.	Calculated for $SeCl_4$.
Se.. ..	35·95	35·79	35·83
Cl.. ..	64·51	—	64·17

Selenium Dioxide and Sulphuryl Chloride.—When these two substances are brought together, no reaction takes place even at elevated temperatures or under strong pressure. Several tubes containing these substances were allowed to stand for a year, but at the end of this time no reaction had taken place. The two when heated together in tubes of very heavy glass, which had been obtained for work of this character, would not react, all of the tubes exploding when the temperature was sufficiently raised, but without previously showing any signs of change in the contents. After numerous attempts to bring the two to react the dioxide of selenium was vaporised from a porcelain boat in a glass tube in the vapour of sulphuryl

chloride, and was condensed in a cooler portion of the tube. Analysis of the sublimed dioxide showed it to be chlorine-free, thus showing that it is possible to sublime selenium dioxide in the vapour of sulphuryl chloride without any reaction taking place. — *Journal of the American Chemical Society*, xxix., No. 1.

THE ATOMIC WEIGHT OF CHLORINE.*

By WILLIAM A. NOYES and H. C. P. WEBER.

(Concluded from p. 149).

Errors and Corrections.

Hydrogen.—If there were any errors due to a contamination of the hydrogen they are not apparent. The hydrogen was prepared and purified with all possible precaution. It was repeatedly tested for impurities in the work on hydrogen and oxygen, and none or only negligible quantities found (Noyes, *Journ. Am. Chem. Soc.*, xxix., 1724).

Two corrections on the weight of hydrogen were found necessary. The first of these was the amount of hydrogen remaining in the chlorplatinate tube at the end of the determination, and pumped out with the residual gases to be analysed. In eight cases out of the twelve this correction was applied, the maximum being 0·11 mgrm., the minimum 0·01 mgrm., and the average 0·047 mgrm. The determinations affected are 1, 2, 4, 5, 6, 7, 11, and 12. The second correction was due to hydrochloric acid in the palladium tube. Under certain conditions, when the current of hydrogen from the palladium tube was not sufficiently rapid, hydrochloric acid found its way back into the palladium tube, either by diffusion or by being drawn back. Correction for this was readily applied. After having been weighed, the hydrogen apparatus was charged for the succeeding determination. The tube was fitted with a stopcock at both ends, as may be seen in the photograph. After the palladium had been saturated with hydrogen the stopcock farthest from the hydrogen generator was connected to a Liebig flask containing water coloured by a drop of methyl-orange. The stopcock at A was opened while the hydrogen generator was kept going, and the hydrogen bubbled through this water before escaping. If the presence of hydrochloric acid made itself known, the palladium was heated to 160° to expel the larger part of the hydrogen it had absorbed, and with it any hydrochloric acid present. It was then allowed to cool with a current of hydrogen passing through it, and finally filled again at normal temperatures. The hydrochloric acid absorbed by the water was then titrated by N/10 sodium or barium hydroxide. The real weight of the hydrogen was greater than the apparent loss of the tube by the weight of hydrochloric acid found. This correction was applied in determinations 1, 3, 4. 10, and 11, varying between 0·35 and 9·26 mgrms. and averaging 4·8 mgrms.

Chlorine from the Loss of the Platinum Tube.—The purity of the chlorine entering into the composition of the chlorplatinate has been spoken of. The maximum amount of bromine in the ingredients used seems to have been 1 in 50,000. The resultant error in the weight would be half of this, since 35·5 grms. are replaced by 80, or 1 : 100,000. There seems to be ample justification for considering this point beyond question.

The only other impurities which could possibly affect the results were volatile products in the platinum or elements capable of producing volatile products, such as ammonia, water, hydroxyl, or oxygen. The method of preparation seems to preclude the possibility of the presence of ammonium salts. The potassium chloride was especially treated to free it from these. Following this there was repeated treatment with chlorine in hot solution. The final heating of the chlorplatinate to 400° over an extended period of time must have caused the destruction and removal of any ammonium compounds which had escaped previous treatment.

The three following impurities, water, hydroxyl, or oxygen in the platinum salt, were somewhat more difficult of treatment. It is known that potassium chlorplatinate hydrolyses in aqueous solution. With this point in view the precipitation of potassium chlorplatinate was carried out in concentrated solutions with both an excess of potassium chloride and hydrochloric acid, and the mother-liquor was removed as soon as practicable. It was shown that by heating sufficiently long at 400°, all occluded hydrochloric acid could be removed, the chlorplatinate being perfectly neutral after this treatment. This served as indirect evidence that the water was also removed. The agreement between Series 1 and 2 may be considered as additional evidence on this point. In the first series the chlorplatinate had opportunity to become saturated with water vapour at the temperature of 350° during the course of the experiment. In the second series it was in equilibrium with solid hydrochloric acid at − 180°. Now hydrochloric acid with its well-known affinity for water vapour may be considered as a very perfect drying agent. Yet the difference between the two series is 1 in 10,000. 120 grms. of potassium chlorplatinate were used. The presence of 0·05 per cent moisture in this salt would have raised the atomic weight of chlorine found from 35·184 to 35·244.

Further, in the second series it was noticed that if the condensation tube for the hydrochloric acid was allowed to contain a trace of moisture before the determination was begun this would remain as a trace of aqueous hydrochloric acid after the gas had been transferred from this part of the apparatus to the absorption bulb, the temperature during this transfer remaining, of course, below zero. If, however, the condensation tube was perfectly dry to start with, no such trace of aqueous hydrochloric acid remained; that is, no water had been carried over from the chlorplatinate.

A final test of the chlorplatinate was made for water, hydroxyl, or oxygen. 100 grms. of potassium chlorplatinate were treated exactly as for a determination. The chlorplatinate was heated to 400° in a current of dry air, transferred to the apparatus used in the determinations, and then evacuated at 350°. Next, pure hydrogen was led over the chlorplatinate until it was completely reduced. The hydrochloric acid formed was led through a narrow U-tube surrounded by a mixture of solid carbon dioxide and alcohol (− 78°). Finally, the whole apparatus, including the U-tube, was evacuated, the final conditions being, 350° in the chlorplatinate tube, − 78° in the U-tube, and several thousandths mm. pressure. Upon weighing, the U tube had shown an increase in weight of 0·9 mgrm. or 1 in 30,000 on the hydrochloric acid formed.

A number of corrections on the weight of the chlorplatinate tube were necessary. The first of these was necessary on account of the traces of air or nitrogen found in the chlorplatinate tube at the end of the determination. These corrections were found necessary in Experiments 4, 5, 6, and 7, their magnitude being 0·35, 0·76, 0·25, and 2 mgrm. This air may have been occluded by the chlorplatinate, or it may have come from the water of the absorption tube. It was immaterial how this correction was applied as it lay within the limits of the experimental errors, the maximum correction being 1 : 10,000.

In the second series it sometimes happened that with the most cautious manipulation, chlorplatinate was blown over into the condensation bulb at the beginning of the experiment. After the hydrochloric acid had been absorbed by the water and the apparatus weighed, this chlorplatinate was removed by dissolving in water, and weighing, first as potassium chlorplatinate and then again as potassium chloride + platinum, after reduction. This correction was applied in Experiments 8, 9, and 11, the amounts being 2·03, 15·0, and 36·5 mgrms. The apparent loss of the chlorplatinate tube was, of course, diminished by these quantities.

Hydrochloric Acid.—From the agreement of Series I. and II. it seems reasonable to assume that no errors were

* From *The Journal of the American Chemical Society*, xxx., No. 1.

introduced by using water as the absorbing agent for the hydrochloric acid.

The corrections on the apparent gain of the absorption tube were of the following nature:—First, the apparent gain was increased by the hydrochloric acid found in the palladium tube, and by the hydrochloric acid pumped out from the chlorplatinate tube. The former has been spoken of under hydrogen. In Experiments 1, 6, and 7 there were found 1·27, 0·8, and 0·15 mgrm. of hydrochloric acid, respectively, in the gases pumped out.

In Experiments, 8, 9, and 11 the gain of the absorption tube was diminished by the amount of the chlorplatinate blown over. The corrections were 2·03, 15·0, and 36·5 mgrms.

The final check on correctness of manipulation, freedom from leaks and other losses, was found in the checking of the sum of the weights of the hydrogen and chlorine with the weight of the hydrochloric acid. In the preliminary experiments of both series, discrepancies were found until the details of the determination had been mastered. On this account and on account of other known errors the preliminary determinations were rejected entirely.

Results.

The values obtained are given in the following tables. The weights represent those found after all correction had been applied. The second part of Experiment 5 was lost.

The value as found for the atomic weight of chlorine is 35·184 with a probable error of ±0·0013. The value obtained for the molecular weight of hydrochloric acid is 36·184 with a probable error of ±0·0012. The combined average of both sections of the two series is 35·184 with a probable error of ±0·0008. This is, of course, on the basis of hydrogen = 1.

	Hydrogen.	Chlorine.	Hydrochloric acid.	At. wt. Cl.	Mol. wt. HCl.
1.	0·25394	8·93293	9·18695	35·177	36·178
2.	0·28004	9·85590	10·13259	35·195	36·183
3.	0·51821	18·23468	18·75359	35·188	36·189
4.	0·67631	23·79587	24·47123	35·186	36·185
5.	0·58225	20·48158	—	35·177	—
6.	0·47989	16·88423	17·36310	35·184	36·182
7.	0·64132	22·55816	23·20054	35·175	36·176
	Average of Series I. ..			35·183 and	36·181
8.	0·81608	28·71691	29·53167	35·188	36·187
9.	0·83194	29·28055	30·11207	35·195	36·195
10.	0·39074	13·74926	14·14078	35·187	36·188
11.	0·75560	26·58427	27·33926	35·183	36·182
12.	0·77518	27·26746	28·04110	35·177	36·175
	Average of Series II. ..			35·186 and	36·185
	Total average			35·184(3)	36·183(7)

On the oxygen basis this value becomes 35·452 if H = 1·00762 (Morley's value) and 35·461 if H = 1·00787 (Noyes' recent value). The values for silver calculated from Richards's ratio and these two values are, respectively, 107·87 and 107·89.

Note.—The values calculated from the results of Dixon and Edgar in the same manner are 35·463 or 35·472 for chlorine and 107·90 or 107·93 for silver. The mean values 35·467 and 107·91 must be considered, for the present, as the most probable which can be calculated from their work. The values for silver are calculated from the results of Richards and Wells (*Journ. Am. Chem. Soc.*, xxvii., 525), who found that 100 parts of silver gave 132·867 parts of silver chloride.

The mean values must be considered as most probable at the present time. These are 35·457 for chlorine and 107·88 for silver.

In eleven experiments 6·41925 grms. of hydrogen were united with 225·86017 grms. of chlorine, and yielded 232·27288 grms. of hydrochloric acid. The values obtained from these figures are 35·1846 and 36·1838.

	H+Cl.	HCl.	Difference.
1.	9·18687	9·18695	+0·00008
2.	10·13594	10·13259	−0·00335
3.	18·75289	18·75359	+0·00070
4.	24·47218	24·47123	−0·00095
6.	17·36412	17·36310	−0·00102
7.	23·19948	23·20054	+0·00106
8.	29·53299	29·53167	−0·00132
9.	30·11249	30·11207	−0·00042
10.	14·14000	14·14078	+0·00078
11.	27·33982	27·33926	−0·00056
12.	28·04264	28·04110	−0·00154
	232·27942	232·27288	−0·00654

It may be interesting to note the discrepancies between the weights of hydrogen and chlorine and the hydrochloric acid formed in the individual experiments.

In these eleven experiments there are seven with an apparent loss of weight, and four with an apparent gain, the total loss being 1 in 35,000.

REVISIONS OF THE THEORY OF ELECTROLYSIS.*

By HENRY S. CARHART, LL.D

(Concluded from p. 152).

Grotthus conceived of the motion of the part-molecules as taking place under electric force only by the progressive exchange of partners in a polarised chain of molecules. Clausius rejected the fixed equilibrium in the normal condition of an electrolyte, and assumed some free part-molecules or, as Faraday named them, ions; and the dissociation imagined by Clausius may be described as temporary, or a continuous exchange of partners in chemical association. Williamson as early as 1851 declared "that in an aggregate of the molecules of every compound a constant interchange between the elements contained in them is taking place." This view Clausius rejected. The assumption that only a few of the molecules in a solution are dissociated into ions appeared to him to satisfy the facts of electrolysis.

The first attempt to answer the question as to the manner in which the facts of electrical conductivity are reconciled with those of general chemistry was contained in the theory of Grotthus; the second attempt was made by Clausius in 1857, and thirty years later a further answer was made in the work of Arrhenius.

Another question relates to the intimate relation between the passage of electricity through an electrolyte and the simultaneous motion of the ions, the ponderable attendant of the electrical transfer. The law of Faraday paved the way for an answer to this question; the reply of the present is largely the work of Hittorf and Kohlrausch.

The simplest statement of Faraday's discovery in electrolysis is that the passage of a fixed quantity of electricity is always associated with the transfer of a grm. equivalent of the ion. The passage through an electrolyte of 96,550 coulombs of electricity always releases or deposits a grm. equivalent of an ion; that is, a grm. molecule of an ion whose valence is one, or half a grm. molecule of an ion whose valence is two. This law demonstrates that there is a fixed minimum, called by Helmholtz *the atomic charge*, conveyed by univalent ions, others conveying only integral multiples of this charge.

The researches of Hittorf on the migration of ions demonstrated that the observed change in concentration at the electrodes during electrolysis makes it necessary to assign to the positive and negative ions different velocities.

* Presidential Address delivered at the Seventh General Meeting of the American Electro-chemical Society. From the *Smithsonian Report* for 1906, p. 147.

Hittorf's work, though of fundamental importance, commanded but little attention at the time of its publication. In fact, it was opposed by the leaders of physical science and was not accepted till thirty years later.

Let me now recount several steps in the revision of electrolytic theory.

Grotthus supposed "that at the moment of the segregated appearance of the hydrogen and oxygen there takes place a division of their natural electricity, either by their contact or by mutual friction, so that the former assumes the positive, the latter the negative condition," and that the links of his chain exchanged partners in such a way as to leave only the end links free.

Clausius assumed "that the ions are not permanently united with each other; that part of them exist in the liquid in an uncombined state, wandering about seeking partners." The electric force imposes on all free ions a uniform drift. To Clausius, therefore, should be assigned the introduction of the theory of dissociation to explain electrolysis. But the dissociation of Clausius was only slight and was conceived to be the accompaniment of a shifting and unstable equilibrium.

Scientific judgment respecting the assumption of Clausius remained in abeyance for thirty years, when Arrhenius published his celebrated memoir on "The Dissociation of Substances Dissolved in Water." An intermediate step, not originally devoted to the theory of dissociation, was van 't Hoff's paper on "The Rôle of Osmotic Pressure in the Analogy between Solutions and Gases." The significant feature of this paper is the generalisation of Avogadro's law to the effect that—

"The pressure which a gas exerts at a given temperature if a definite number of molecules is contained in a definite volume is equal to the osmotic pressure which is produced by *most substances* under the same conditions if they are dissolved in any given liquid."

The major part of van 't Hoff's paper deals with non-electrolytes or organic compounds, such as a solution of sugar, which show little or no deviation from Avogadro's law as applied to osmotic pressure. When he alludes to those substances which exhibit abnormally large osmotic pressure, he acknowledges his indebtedness to the personal suggestion of Arrhenius to the effect that the solutions obeying the law of Avogadro are non-conductors of electricity, a fact indicating that they are not broken down into ions, while solutions which give higher values of the osmotic pressure than accord with the laws of gases are all electrolytes. But if these suffer partial dissociation in solution, then the number of particles is increased, each ion contributing to the pressure as much as a complete molecule. The excessive osmotic pressure is thus accounted for.

Arrhenius divided the molecules in a conducting solution into active and inactive portions. The former are those whose ions are independent of one another in their movements; the latter are the remaining molecules whose ions are firmly bound to each other, and the ratio between the two he called "the activity coefficient."

The significant conclusions of Arrhenius are:—

1. "That van 't Hoff's law holds not only for *most*, but for *all substances*, even for those which have hitherto been regarded as exceptions (electrolytes in aqueous solution)."

2. "That every electrolyte (in aqueous solution) consists partly of active (in electrical and chemical relation) and partly of inactive molecules, the latter passing into active molecules on increasing the dilution, so that in infinitely dilute solutions only active molecules exist."

The ratio of the active to the inactive molecules, or the activity coefficient, is intimately connected with the electrical conductivity of solutions. Molecules dissociated into ions are alone capable of conducting or conveying electricity through a solution. The inactive molecules are at best only inert and take no part in the electrical transport. The activity coefficient increases with the dilution—that is, the molecular conductivity, which expresses essentially the conductance of a given number of molecules in solution, is greatest when the dilution is such that all molecules of the solute are dissociated. This is the essential significance of the researches on electrolytic conductivity, so far as they bear on the theory of electrolysis.

The transition from the incidental and almost infinitesimal dissociation assumed by Clausius to the ideal infinite dilution and complete dissociation taught by the "Leipzig School" marks the essential revision of the theory of electrolysis made in recent years.

The theory of ionisation has now passed beyond the bounds of electrolytic solutions. As van 't Hoff imported the gas law into solutions to explain osmotic pressure, so others, like J. J. Thomson, have seized on electric convection by ions to explain electrical discharges through gases. It is now conceded that the only tenable explanation of electric currents through gases is that of convection by ions. The ionisation of gases is brought about by ultra-violet light, by Röntgen rays, and by the radiations from radio-active substances. The electric charge conveyed by ions in gases appears to be identical with the charge conveyed by ions in an electrolyte in aqueous solution, but the masses conveying negative charges are only about the one-thousandth part of the hydrogen ion.

The passage of electricity through a gas, as well as through an electrolyte, is accompanied by chemical changes; and chemical decomposition, says J. J. Thomson, is not to be considered an accidental attendant on the electrical discharge, but an essential feature without which it could not occur.

In reviewing the changes that have occurred in the theory of electrolysis I would not be understood to imply that we now have the ultimate truth. Many cogent objections have been urged against the theory of dissociation in its present form. Theories should be regarded as helps or scaffolds only; they are necessary for the construction of the edifice of truth, and they finally disappear like the staging. We should use them as temporary expedients, not retaining them till the whole edifice is completed, but only until a grand arch is finished, some minaret or tower emerges against a clear sky or light streams through some noble window.

The physicist or chemist who is more intent to ascertain the truth than to preserve inconsistency, holds to a theory no longer than he finds it able to furnish support. Faraday, the prince of research, said that experimental work is a great disturber of preconceived theories.

Just now the dissociation theory is in a state of siege, with many valiant defenders. The objection is urged that there are many cases of electrolytes in solution in which the osmotic pressure does not exceed that required by the gas law. Hence, there can be no dissociation. Also that the simplest cases of electrolysis are those of a molten salt, such as silver electrodes in molten silver chloride. In these cases there is no complication with a solvent and no dissociation by solution. In what way, then, is that migratory freedom of the electrically charged part-molecules, which is assumed in the theory of dissociation, secured in a molten salt? Doctor Kahlenberg has shown that "a normal solution of trichloracetic acid in allyl mustard oil is a poorer conductor of electricity than the purest water which Kohlrausch ever prepared in contact with air, and yet this solution attacks dry magnesium rapidly, and decomposes dry carbonates of sodium and potassium." But chemical reactions are assumed to depend on dissociation into ions, as does electrical conductivity.

This much is generally accepted: "The ions must be free to move; but this migratory freedom may be secured either by ionic interchanges between the molecules, as Clausius imagined, or by a prolonged separation in accordance with the dissociation hypothesis of Arrhenius and Planck. The essential point in the general ionic theory is the migratory freedom."

The solution of obscure problems, like those of electrolysis, in which event the chief agent itself is an elusive

enigma, is necessarily one of prolonged effort, with many a flamboyant processional and the not infrequent refrain of the later recessional. But there is no occasion for discouragement, for we are destined to struggle for ever with the unsolved problems of the here and the hereafter.

It is often darkest just before the dawn. Sometimes, too, we emerge into the light with a suddenness that blinds before the eye adjusts itself to the new illumination. One dreary day in April I took the train in Switzerland over the St. Gothard route. We entered the north end of the tunnel at Goeschenen with a clouded sky and snowflakes swirling through the air. Ten minutes passed in the darkness a thousand feet beneath the village of Andermatt —fifteen, seventeen, and then the train ran out on the Italian side of the great divide at Airola into a burst of sunshine and clear sky and white-capped Alpine peaks and tempered winds and the pale green of olive groves. So sudden was the transformation that an involuntary exclamation of surprise and delight ran through the train. The experiences of the last twenty years warn us that we must be prepared for similar surprises in the illumination that physical science is shedding on the world of nature. We need not prophesy; we need only work and wait.

AN EXPERIMENTAL INVESTIGATION OF THE NATURE OF THE γ-RAYS.*

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In papers recently published in the *Proceedings of the Royal Society of South Australia* (May and June, 1907) and in the *Philosophical Magazine* (October, 1907) an attempt was made to show that the ether-pulse theory of γ- and X-rays might prove to be incorrect after all, and that most of the known properties of these rays could be explained more simply and directly on the supposition that they were material and consisted of neutral pairs. The arguments were based on comparison of known phenomena with deductions from each of the two opposing hypotheses. At that time there did not seem to be any opportunity of appeal to a decisive experiment.

The object of this paper is to give a preliminary account of an investigation which appears to us to give a final answer as regards the γ-rays, and to show that they are material in nature.

Secondary radiation, which is excited in an atom by a passing wave or pulse, must be distributed symmetrically with regard to a plane passing through the atom perpendicular to the direction of motion of the pulse. If we speak of the primary pulse as going forwards, the secondary radiation is just as likely to go backwards as forwards. This is a well-recognised principle. For example, J. J. Thomson divides the secondary radiation, due to γ-rays, into two equal parts, which he supposes to move away symmetrically in opposite directions, and, for convenience of calculation, parallel to the direction of the primary rays ("Conduction of Electricity through Gases," p. 406). Supposing, therefore, a pencil of γ-rays to pass normally through a plate so thin that its absorption may be neglected, the secondary radiation should be exactly the same on the two sides of the plate—in amount, in quality, and in distribution; and it ought not to be possible to discover, by any comparison of the secondary radiations on the two sides, which is the face of entry and which of emergence.

Consider now the ionisation-chamber represented in Fig. 1. The two ends are closed by plates, of which A and A′ are alike; so also are B and B′. The substance of A and A′ is different to that of B and B′. The nature of the side walls is immaterial. A pencil of γ-rays passes along the axis of the chamber, which is represented by a dotted line. The ionisation current within the chamber is measured as usual by inserting a high potential electrode connected to an electroscope.

When the plates A and B are inverted, there is a change in the amount of the current; so also when A′ and B′ are inverted. By an extension of the principle already stated, it ought not to be possible, on the ether-pulse theory, to

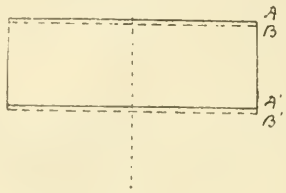


Fig. 1.

discover which way the rays are going, up or down, in the figure, by comparing the consequence of inverting A and B with that of inverting A′ and B′.

As a matter of fact, the direction can be discovered with ease; the more easily the greater the difference between the atomic weights of A and B.

For example, in one experiment of ours the chamber was of cylindrical form, 3 inches high and 10 inches diameter. The plates used were of aluminium and lead. The thickness of each plate was a little less than 2 mm. Inversion of the top plates A and B made a difference in favour of Al of less than 1 per cent, *i.e.*, the current was slightly larger when Al was next the chamber. On the

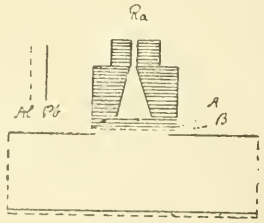


Fig. 2

other hand, inversion of the bottom plates made a difference of 44 per cent in favour of Pb, *i.e.*, the current was 44 per cent larger when the Pb was on top. The details are shown in the figure. Allowance was made for all radiation other than that which proceeded down the conical opening in the lead block.

It may be well to point out that this effect cannot be ascribed to any complication due to secondary or tertiary rays. No doubt the radiation in the chamber is very complex; but the fact is immaterial. Provided that the chamber is symmetrical in the first place, then the secondaries must be symmetrical also if the ether-pulse theory is correct, and therefore the tertiaries and so on. Nor is it necessary to consider whether the secondary radiations are β-rays or scattered γ-rays. Also, it must be remembered that the secondary radiations which enter the chamber have their origin almost entirely in a very few millimetres of material bordering on the chamber. Therefore, the γ-rays are in almost exactly the same condition, both as to quality and as to quantity, when they excite secondary radiations from the top plate as they enter the chamber, and secondary radiations from the bottom plate as they leave.

The details of the experiment may be varied greatly; but in all the cases we have tried the want of symmetry is obvious. In Fig. 3 are shown the details of one other case, in which carbon and lead were the materials used, and the form of the chamber was different. It seems

* From the *Transactions of the Royal Society of South Australia*, 1908, xxxii.

unnecessary to give more, because, in the first place, the experiments are easy to repeat; and in the second place, the complete quantitative analysis of the figures depends on several factors, the influence of which is imperfectly understood, such as the previous screening of the rays, the form of the chamber, and the respective parts played by the

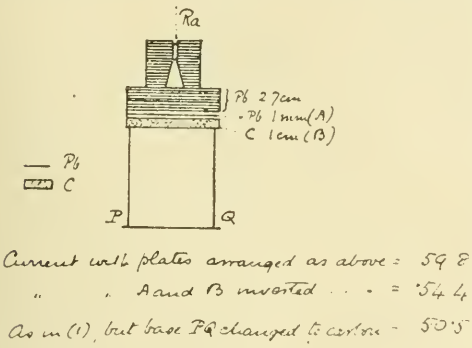

Ra
Pb 2·7cm
Pb 1mm(A)
C 1cm(B)
Pb
C
P
Q
(1) Current with plates arranged as above = 59 8
2) " A and B inverted . . = 54 4
3) As in (1), but base PQ changed to carbon = 50·5

Fig. 3.

original γ-rays, cathode rays, and secondary γ-rays, if any such exist. The experiments, as they stand, show how far away is that symmetry which the ether-pulse theory demands. It seems to us that there is no escape from the conclusion that the γ-rays are not ether-pulses.

Let us, therefore, proceed to consider the hypothesis that the γ-rays are material. In the paper already mentioned, it was argued that they might well consist of neutral pairs, liable to be broken up on encountering atoms or parts of atoms; and that the secondary cathode radiations might be the negative particles thus set free. Let us suppose, provisionally, that the particles, when set free, move at first in the direction of the γ stream, but are subsequently scattered in the usual manner of β-rays. (It is here that the absence of symmetry arises. On the pulse theory the particles should go equally backwards and forwards; indeed, if they were ejected by atomic explosions, the result of energy accumulated from passing pulses, as suggested by J. J. Thomson in the case of X-rays, they would move equally in all directions).

Wigger gives a table (*Jahrbuch der Radioaktivität*, Bd. ii., p. 431) showing that the γ-rays are absorbed according to a density law pretty strictly, except for small thicknesses of substances of large atomic weight.

Assume this law to hold good, and also assume for the present that the absorption of β-rays follows the density law. The latter is only roughly true, of course; but we may deal with quantities in a broad fashion first, and

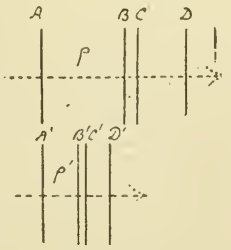


Fig. 4.

make the proper amendments afterwards. We can now compare the quantities of cathode radiation which should emerge from the far sides of two plates of different densities ρ and ρ'. Let these be represented by AD and A′D′ in the figure, and let BC and B′C′ be corresponding strata of equal weight; in fact, let $AB/A'B' = BC/B'C' = CD/C'D' = \rho'/\rho$. Let the plates be crossed by equal pencils of γ-rays, as shown in Fig. 4. A certain quantity of γ radiation is absorbed in crossing BC. In the language of our present hypothesis we should say that a certain number of γ particles are stripped of their positives, and the negative remainders go on. An equal number of negatives are set free in B′C′ because the two strata are of equal weight. Of those set free in BC only a certain number emerge from the face D, because of the absorption of the plate CD. Since CD and C′D′ are of equal weight, a similar absorption occurs in the case of the particles set free in B′C′. Thus the same number emerge from each plate. Integrating for all effective strata, the whole cathode radiations emerging from the two plates are equal.

We thus find that if the absorption of β- and γ-rays both followed the density law, the secondary cathode radiation on the far side of a plate—we may call it the "emergence" radiation—would be the same for all materials. There should be no such relation between the amount of the radiation and the atomic weight of the plate, as various observers have shown to be true for the secondary cathode radiation of "incidence," a relation which is closely parallel to that found in the case of β-rays.

Experiment is in agreement with this theory, for it shows that no such relation exists in respect to the emergence radiations; in marked contrast to what happens in the case of the radiations from the front sides of plates of various materials, the incidence radiations.

It is true that the emergence radiations are not all equal, but this is to be expected, because (1) the amount of secondary cathode radiation depends, as Kleeman has shown, on the previous screening of the γ-rays; (2) the β-rays are not absorbed strictly according to a density law; (3) the γ-rays also depart from this law. We have made no serious attempt as yet to disentangle the effects of these various disturbing factors. In fact, the task promises to be long and intricate, for it will be necessary to find out how much of the ionisation in the chamber is due to each class of rays; to discover the law of distribution of the radiations in space, so that the form of the chamber may be allowed for, if necessary; to find out the nature of the departures from the density law of those β- and γ-rays which are in question; and so on. Nevertheless, the results are satisfactory, so far as we have gone. The amount of emergence radiation is found to depend on the previous screening of the rays. In one case the inversion of a C—Pb pair of plates from C—Pb to Pb—C, altered the current in the ratio 1 : 1·11 when the rays had been previously screened by Pb; but in the ratio 1 : 0·96 when the screen was changed to C. Again, when the rays had previously passed through an iron screen, the inversion Pb—Fe to Fe—Pb changed the current in the proportion 1 : 1·12, but when a lead screen was substituted for an iron one the change was 1 : 1·04. In illustration of the effect of the second disturbing factor mentioned above, we have found that, other things being equal, the substances of small atomic weight give the most secondary radiation, in a general way; and it may be no coincidence that in some cases we have found Sn and Fe to give surprisingly small amounts. This is in agreement with what is to be expected, for it is clear, on consideration of the argument already given, that the greater the β-ray absorption of a substance in proportion to its density, the less "emergence" radiation should issue from it. Some observers have found Sn and Fe to possess exceptional absorbing powers. We do not wish, however, to lay any stress upon these last observations, some of which we may not have interpreted correctly; but we mention them in order to show that the inequalities that are found to exist between the emergence radiations of various substances promise to be reducible to order as soon as the difficulties of interpretation have been surmounted.

Let us now consider the cathode radiations on the front sides of the plates. Of the cathode particles set free in BC and moving at first in the direction of the γ-rays, a certain proportion, say p, is returned by what is beyond.

These move towards the face A, and a certain number of them succeed in reaching it and emerging therefrom. In the case of the other plate the proportion returned is p'. The absorption in B'A' is the same as in BA, because the weights are the same. Comparing the two plates, stratum by stratum, we find that the "incidence" radiation of one plate is to the incidence radiation of the other plate as p to p'. Now p and p' are the well-known constants of the β-rays.

When a stream of γ-rays is allowed to fall upon a plate the cathode radiation which issues from the place of incidence must be divisible into two parts. One consists of scattered β particles derived from the stream of such particles which was travelling with the γ-rays before incidence, and which was formed during the previous transit of the screens employed, solid, liquid, or gaseous. This part is scattered to an extent which depends on the atomic weight of the plate, according to the usual law of β-particles. The other part is originated in the plate itself in the manner just described, and the amount of it is also regulated according to the β-ray law. When, therefore, observers have measured the secondary radiation, due to γ-rays, and have found a law corresponding to that for β-rays, the reason of the correspondence has been that they really were measuring the secondary radiation due to β-rays. Properly speaking, the secondary radiation, produced by γ-rays, or, rather, *from* γ-rays, is proportional to the density of the substance traversed (*cf.*, Wigger's table), and this is only another form of the law of absorption of γ-rays.

The relative importance of the two parts of the incidence radiation just mentioned must depend on the circumstances of the experiment. (In a recent letter addressed by one of us to *Nature*, too great a preponderance was assigned to the first part under all circumstances). The researches of Kleeman (*Phil. Mag.*, Nov., 1907) show very well how the second part, which is influenced by previous screening, modifies the effect of the first part, which is not so influenced, but which follows the law of β-rays strictly.

It is easy to show, by comparing corresponding strata at the front and back of one plate, that the incidence radiation should be somewhat less than p times the transmitted radiation. Somewhat less, because the cathode radiation, which is turned back, is scattered and softened in the process.

To sum up:—On the ether-pulse theory we ought to find perfect symmetry in the secondary radiations from the two sides of a plate. But experiment shows nothing of the kind.

On the material or neutral-pair theory, the "incidence" radiations should follow the β-ray law. This is known to be the case. The emergence radiations should not follow the β-ray law, and experiment shows that they do not. If the density law held for both β- and γ-rays, and if the γ-rays were homogeneous, the emergence radiations should all be equal. As already explained, experiment shows that the observed inequalities give promise of ready explanation, on the ground that no one of these suppositions is quite true.

It is, perhaps, better not to extend the preliminary account of these experiments by any lengthy discussion of the issues arising from them. Many points that invite consideration have been discussed already in the papers first referred to. Moreover our own further experiments are incomplete, and their full interpretation is not yet certain. We will, therefore, confine ourselves to one or two questions which seem of special interest. The X-rays resemble the γ-rays so closely that it is practically inconceivable that the two radiations should be essentially different. The secondary cathode radiations, which are set free when X-rays impinge on any material, must therefore have been part of the X-ray stream, and must start their independent existence by moving on in the line of the X-ray motion. Their velocity is much smaller than that of the secondary cathode rays due to γ-rays, and they are much more readily scattered. It may still remain an open question whether or no the X-ray stream contains ether pulses. Perhaps their existence must be supposed in order to explain the velocity experiment of Marx, and the diffraction experiment of Haga and Windt. Possibly they are also required in order to explain Barkla's polarisation experiments; but we do not think that the experiment described by Barkla in *Nature* (October 31, 1907) is in any way decisive.

It seems proper to consider a possibility that the negative particle, when it moves on in the original line of motion of the pair from which it came, retains also its original velocity. It is a striking fact that the cathode particle, due to the γ-rays, has the same speed, very nearly, as the β particle issuing from the original radio-active material. And it looks quite unlike a coincidence that similar comparisons can be made in the case of the X-rays. The secondary cathode radiations due to these rays have velocities which, at the least, are of the same order as the velocities of the cathode particles in the X-ray bulb. If we examine the table given by Innes (*Proc. Royal Soc.*, Aug. 2, 1907, p. 461), and if we may be allowed to adopt an interpretation differing somewhat from the author's, but more natural, it seems to us, in view of the conclusions of this paper, we find that the velocities of the electrons emitted by all the metals are practically the same, zinc being an exception, because it is unable to break up the hardest rays. We find that the velocities range from about 6×10^9 to $7{\cdot}5 \times 10^9$ for soft rays, and 6×10^9 to 8×10^9 for hard rays. Remembering that bundles of X-rays are very heterogeneous, the natural conclusion seems to be that the softest rays give the slowest speeds, and that the velocity of the secondary rays increases with the hardness of the X-rays from which they are derived. (By independent experiment, Bestelmeyer, *Ann. der Phys.*, 1907, xxii., p. 429; and Cooksey, *Am. Journ. Sci.*, Oct., 1907, arrive at the same conclusion). Now the hardness of the rays grows with the speed of the cathode particles in the bulb. Is it then possible that the cathode particle is first set in motion by the electromotive force in the bulb, strikes the anticathode, and picks up a positive there, becomes neutral, and is now called an X-ray, is subsequently stripped of the positive, and becomes a secondary cathode particle, the identity of the negative remaining the same throughout, and its speed invariable, or nearly so? The difficulty comes in when we try to consider the part played by the mass of the positive. Probably it becomes necessary to consider it as small compared to the mass of the negative. In many ways such a supposition would fit in very well. We should then understand why the positive is so hard to isolate: also a radio-active atom, in ejecting a γ-particle would not lose appreciably in weight. Lilienfeld believes he has found the positive electron to be less massive than the negative (*Deutsch. Phys. Gesell. Verh.*, 9, 7, April 15, 1907).

And, again, may not the β and γ forms be interchangeable at times? A γ-particle, which had been stripped of its positive, and become a secondary cathode, or β-ray, would be lost to measurement as a γ-ray; and we should thus have an explanation of how the γ-rays are "absorbed," and why the absorption follows an exponential law. And in the same way, if a β-particle picked up a positive, it would disappear from view as a β-particle, it would be "absorbed."

Although we have made a few experiments with magnetic fields, we have not yet come to any conclusions as to whether or no there are γ pairs which have become loosened in the attachment of positive to negative, forming a softer and more ionising radiation. Their existence might be suspected since there is an analogous effect in the case of X-rays; and probably they would be found more at the back of the penetrated plate than in front of it.

A few further experimental illustrations are shown diagrammatically in Figs. 5, 6, and 7.

The upper part of Fig. 5 shows the general arrangement,

The lower figures are diagrammatic, and show the currents for different arrangements of the Pb and Al at the bottom of the chamber, and at the top, with the exception of the plate through which the γ-rays enter. Inverting the top plates makes little difference where the upper of the two

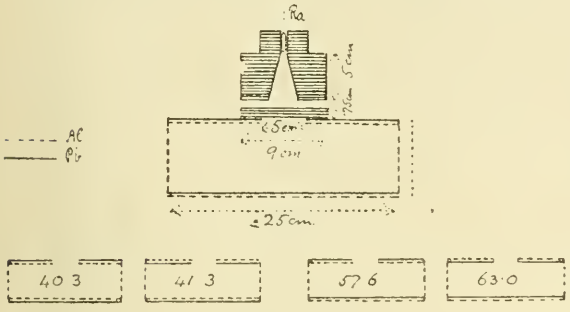


Fig. 5.

plates at the bottom is Al, but an appreciable difference when it is Pb, because in the latter case a good deal of secondary radiation is thrown upwards by the Pb, and there is a tertiary from the top plate.

The same, when the conical opening is completely filled by a Pb stopper:—

12·6 12·6 17·7 18·3

The differences show the effects of those rays only which which do not pass through the Pb stopper:—

27·7 28·7 39·9 44·7

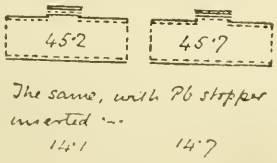


Fig. 6.

Fig. 6 shows the effect of inverting that portion only of the top plate where the γ-rays enter. Three Pb plates = 0·55 cm., Al plate = 0·16 cm.

The upper part of Fig. 7 shows the general arrangement. The wall of the cylindrical vessel was of brass; a Pb or an Al lining could be inserted as shown. The lower

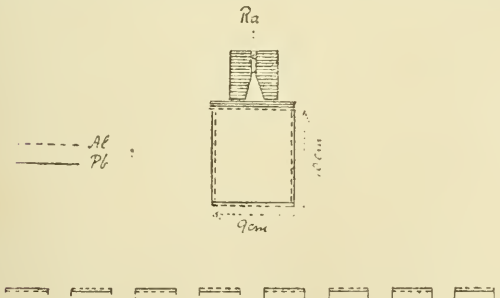


Fig. 7.

figures are diagrammatic, and show the currents for different arrangements of Pb and Al at top, bottom, and sides. Inversion of the plates, *through* which the γ-rays pass into the chamber, makes little difference; but there is a great alteration if the material is changed on which the γ-rays fall, or the emergence radiation from the top plate. The base is of less importance than in Fig. 5; but the sides of more importance. This should clearly be so, for geometrical reasons.

When the conical opening was filled by a Pb stopper, the currents were all reduced considerably, but retained the same proportions pretty nearly.

On the other hand, when a small pencil of β-rays was admitted through a hole in the centre of the top plate, a change of the material of the bottom became more effective, and of the sides less effective than before; but this difference became smaller when thin Al sheets were so placed as to scatter the β-rays on their entry into the chamber.

In conclusion, we should like to add that Wigger was the first, so far as we know, to show clearly that the secondary radiation of Al, on the far side of the plate, might be greater than that of Pb. A comparison of the emergence radiations of different metals was made by Dawes (*Phys. Rev.*, xx., p. 182), who showed that they did not follow the law of the incidence radiations. The same effect was indicated in the experiments of Eve (*Phil. Mag.*, December, 1904). We have little doubt that the interesting experiment of Mackenzie (*Phil. Mag.*, July, 1907) is to be explained on the lines indicated in this paper. In fact, it is clear that this is the case in a broad sense; but it is difficult to give a complete explanation until the laws are so completely worked out that they can be applied to the interpretation of experiments, which are really very complicated, although at first sight they may seem to be simple.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 19th, 1908.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President in the Chair.

MESSRS. W. R. Bousfield, M. J. A. Braun, J. A. Carpenter, T. P. Hilditch, O. Oberländer, A. W. Oke, and T. M. Tyson were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Leonard Clifford Green, B.E., Wienholt Street, Torwood, Brisbane; William Hall, B.Sc., Inglewhite, Manchester Road, Bolton; Hugo Stefan Kohn, Ph.D., 3A, Hythe Road, Willesden Junction; Gerald Roche Lynch, 160, Holland Park Avenue, W.

The PRESIDENT announced that Prof. W. Jackson Pope had expressed himself unwilling to accept nomination for Vice-Presidency.

Of the following papers, those marked * were read:—

*57. "*A New Form of Pyknometer.*" By WILLIAM ROBERT BOUSFIELD.

The author described a new form of pyknometer, intended for very accurate density determinations.

*58. "*The Action of Heat on α-Hydroxycarboxylic Acids.* Part IV. *Racemic αα'-Dihydroxyadipic Acid and Meso-α₁'-dihydroxyadipic Acid.*" By HENRY RONDEL LE SUEUR.

When αα'-dihydroxyadipic acid melting at 146° (compare *Proc.*, 1907, xxiii., 196) is heated above its melting-point, it loses water, and its dilactone (m. p. 134°) is formed as a crystalline sublimate. The acid has been resolved into its optical antipodes by fractional crystallisation of its cinchonidine salt. The *d*-acid melts at 157°, and has $[\alpha]_D$ 16 +3·8°; its *ammonium salt* is lævorotatory, and has $[\alpha]_D$ 11 −21·4°.

When the αα'-dihydroxyadipic acid melting at 174° is heated at 180—190° it loses water, forming a lactone-lactide. All attempts to resolve this acid have failed, and

it must therefore be regarded as the meso- or internally compensated variety.

That the acid which admits of resolution into its optically active components readily forms a dilactone, whereas the meso-variety does not, is in complete agreement with the spacial formulæ of these substances. Characteristic derivatives of both acids have been prepared.

*59. "*The Spontaneous Crystallisation of Sodium Sulphate Solutions.*" By HAROLD HARTLEY, BERNARD MOUAT JONES, and GEORGE ADRIAN HUTCHINSON.

The authors have examined the spontaneous crystallisation of sodium sulphate solutions, and have found that if the solutions are subjected to mechanical friction three of the four possible solid phases, namely, ice, $Na_2SO_4,7H_2O$, and Na_2SO_4, are produced spontaneously at definite temperatures. Supersolubility curves have been traced for these three phases which, in conjunction with the solubility curve, define the labile and metastable regions for the system. The spontaneous crystallisation of the fourth solid phase, $Na_2SO_4,10H_2O$, is of rare occurrence compared with that of $Na_2SO_4,7H_2O$, and seems to take place irregularly without any definite relation to the temperature and concentration of the solution.

*60. "*Constitution of Hydroxyazo-compounds. Action of Diazomethane and of Mercuric Acetate.*" By CLARENCE SMITH and, in part, ALEC DUNCAN MITCHELL.

Diazomethane reacts with *p*-hydroxyazo-compounds to form the methyl ethers obtained by the ordinary methods of alkylation. Benzeneazo-*p*-cresol, *p*-chlorobenzeneazo-*p*-cresol, and β-benzeneazo-α-naphthol do not react with diazomethane.

The action of mercuric acetate in boiling aqueous-alcoholic solution on benzeneazophenol, 2 : 4 : 6-tribromobenzeneazophenol, benzeneazo-*o*-nitrophenol, benzeneazo-*oo'*-dibromophenol, benzeneazo-*p*-cresol, and benzeneazo-*o*-bromo-*p*-cresol has been examined, with the result that the number of mercuriacetate groups entering the molecule of the hydroxyazo-compound is equal to the number of unsubstituted positions in the ortho-position with respect to the oxygen atom. The substances obtained are yellow, red, or reddish brown compounds, readily soluble only in acetic acid, and not melting below 300°, with the exception of benzeneazo-*p*-cresol mercuriacetate, $C_6H_5{\cdot}N_2{\cdot}C_7H_5(OH){\cdot}Hg{\cdot}CO_2{\cdot}CH_3$, which melts at 269—270° with decomposition, and is identical with the compound obtained by Dimroth (*Ber.*, 1902, xxxv., 2864). The corresponding mercurichlorides and mercuribromides have been obtained from the mercuriacetates by means of sodium chloride or potassium bromide in alkaline or acetic acid solution.

DISCUSSION.

Mr. BALY wished to put in a plea for the spectroscopic evidence which so decidedly pointed to the fact that, of the hydroxyazo-compounds, the ortho were quinonehydrazones, whilst the para had the true hydroxyazo-structure. He emphasised the fact that where a possibility of tautomerism existed as in the case under discussion, chemical means failed to determine which of the two possible desmotropic forms a substance possessed. Mr. Tuck had shown that the quinonehydrazone form on the one hand, and the hydroxyazo-form on the other, each represented by compounds, the structure of which was beyond cavil, exhibited two types of spectra which differed very greatly in the relative dilution at which the absorption bands appeared, and also in the shape of the bands themselves. Inasmuch as the parent hydroxyazo-compounds conformed to one or other of these types, so was their constitution in alcoholic solution established, notwithstanding any chemical evidence to the contrary.

It appeared further from Dr. Smith's paper that a slightly different interpretation might be put upon his results. Dr. Smith had pointed out that, in the case of the para-hydroxyazo-compounds, both methyl sulphate and diazomethane introduce a methyl group into the hydroxyl group, thus proving the hydroxyazo-configuration. In the case of the ortho-compound, diazomethane had no action and methyl sulphate only acted at 100°, and then the compounds behaved as if they possessed the hydroxyazo-structure. Again, Dr. Smith had pointed out that his experiments with mercuric acetate were carried out at 85°, but he (the speaker) thought these results rather led one to believe that the para-hydroxyazo-compounds were true hydroxyazo-bodies, but that the ortho-isomerides were quinonehydrazones at the ordinary temperature, and at 100° they tended to favour the hydroxyazo-form. In other words, as the temperature rose the equilibrium between quinonehydrazone and hydroxyazo-forms was shifted towards the hydroxyazo-side, so that at 100° the compounds could react in this form.

Dr. MORGAN said that, in 1889, Prof. Meldola and he had found that benzeneazo-β-naphthol could be benzoylated and ethylated only with some difficulty, and that the products, when mildly reduced in the presence of acids, underwent the benzidine transformation to 4 : 4'-diaminophenylnaphthyl bases which still contained the benzoyl and ethyl groups attached to the phenolic oxygen. They drew from these results the conclusion that the acyl and alkyl derivatives of benzeneazo-β-naphthol were true azo-compounds and not β-naphthaquinonehydrazones. It was interesting to find that the authors held the view that the ortho-hydroxyazo-compounds were really azo- and not hydrazino-derivatives.

The presence of many other constituents, besides the azo-group, in the contiguous α-position greatly modified the properties of β-naphthol or β-naphthylamine, but it was scarcely possible in every instance to ascribe this effect to the existence of a quinonoid configuration.

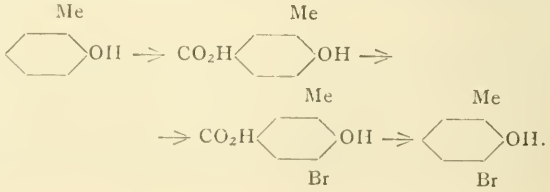
Dr. HEWITT drew attention to the fact that benzeneazo-*p*-cresol behaved as a phenol towards substituting agents even at the ordinary temperature. A cold solution of the substance in glacial acetic acid, containing excess of fused sodium acetate, brominated exclusively in the phenolic nucleus.

It should be remembered that spectrographic evidence, valuable though it was, ultimately depended on the determination of the constitution of typical substances by chemical methods.

Dr. SMITH, in reply, expressed the opinion that the spectrometric evidence by no means conclusively proved the quinonehydrazone structure of *o*-hydroxyazo-compounds and of their acyl derivatives. Benzoquinonebenzoylphenylhydrazone, which was undoubtedly a quinonehydrazone, gave a totally different absorption spectrum from that of the isomeric benzoylbenzeneazophenol, which had the azo-structure, whilst benzoylbenzeneazo-*p*-cresol gave an absorption curve closely resembling that of benzeneazophenol. With regard to the point raised by Mr. Tuck, the reduction of β-benzeneazo-α-naphthyl acetate resulted first in the formation of the hydrazo-compound, then wandering of the acyl group from the oxygen to either of the nitrogen atoms took place, and, finally, fission occurred, yielding the four products, aniline and N-acetyl-2-amino-1-naphthol, acetanilide and 2-amino-1-naphthol.

*61. "*Orthobromophenols and some Bromonitrophenols.*" By PHILIP WILFRED ROBERTSON.

The method of direct bromination cannot be employed for the preparation of *o*-bromo-*o*-cresol or the corresponding *o*-bromoguaiacol. Accordingly, these compounds were obtained by an indirect method, as is indicated in the following scheme illustrating the changes in the case of *o*-cresol :—



The constitution of the *o*-bromo-derivatives was confirmed by the fact that, on nitration, they yielded the same *o*-bromo-*p*-nitrophenols as are obtained from the *p*-nitrophenols by bromination.

o-*Bromo*-p-*nitro*-o-*cresol*, p-*bromo*-o-*nitro*-o-*cresol*, and o-*bromo*-p-*nitroguaiacol* form a red and a yellow series of *potassium* salts, being a confirmation of the recent work of Hantzsch (*Ber.*, 1907, xl., 330).

Bromonitrothymol is anomalous, as only one isomeride (m. p. 109°) is obtained by the reactions: (1) nitration of *p*-bromothymol, (2) bromination of *o*-nitrothymol, (3) nitration of *o*-bromothymol, (4) bromination of *p*-nitrothymol; this isomeride must be o-*bromo*-p-*nitrothymol*, as it forms bromo-*p*-thymoquinone on oxidation.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 7, February 17, 1908.

Lithium in Radio-active Minerals. — Mdlle. Gleditsch. — The author has determined the amount of lithium in certain radio-active minerals spectroscopically by comparing the intensity of lithium lines in the residue, after dissolving the mineral and separating the other constituents, with the intensity of the corresponding lines in artificial mixtures containing lithium. The results obtained were as follows :—

	Copper, per cent.	Lithium, per cent.	Activity referred to uranium.
Joachimstal pitchblende .	1·2	0·00017	1·5
Colorado pitchblende ..	0·15	0·00034	1·75
Carnotite	0·15	0·030	0·52
Cornwall chalcolite ..	6·54	0·00011	2·0
Autunite	—	0·00083	1·48
Thorite	Trace	0·0033	0·59

The relatively large amount of lithium in carnotite is interesting, especially as the mineral contains but little copper. The results obtained do not contradict Ramsay's theory of the transformation of copper into lithium, though they do not support it; they show, however, that there is no simple ratio between the copper and lithium in radio-active minerals.

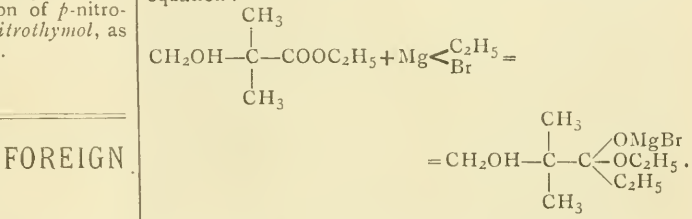
New Method of Determining Sulphur in Organic Matter.—Isidore Bay.—The organic matter is ignited in a combustion tube in presence of sodium carbonate and bromide and calcined magnesia. The contents of the tube are washed out into a dish, dissolved in dilute hydrochloric acid, boiled to drive off the bromine, and filtered. The sulphur in the filtrate is determined as sulphate by adding barium chloride. This method is as accurate as Carius's, and much quicker.

Separation of Silver Chloride and Iodide.—H. Baubigny.—To separate a mixture of silver iodide and chloride the precipitate of the two salts is washed and treated with a solution of commercial ammonium sesquicarbonate at 70—80°. After a few minutes the liquid is allowed to cool and decanted off, and the same treatment is repeated. Finally, the residual iodide is washed on a filter with dilute ammonia. The chloride is separated from its solution by the addition of nitric acid, and is determined in the usual way. This method is more accurate than Hager's process of approximate separation.

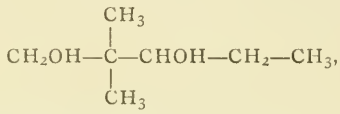
Complete Analysis of Vegetable Matter.—J. M. Albahary.—Already noticed.

Reciprocal Displacement of Hydrocarbon Groups in Friedel and Craft's Reaction.—H. Duval,—When diphenylmethane in cold carbon disulphide solution is subjected to the action of acetyl chloride in presence of aluminium chloride, *p*-*p*-diacetyldiphenylmethane, *p*-monoacetyldiphenylmethane, and a considerable quantity of acetophenone are formed. The latter can result only by the replacement of a C_6H_5—CH_2 group by the group CH_3—CO, under the influence of aluminium chloride.

Reducing Properties of Organo-metallic Compounds. — M. Letellier. — Ethyl magnesium bromide reduces ethyl oxypivalate, as shown by the following equation :—



The product is then further reduced to the glycol,—



with disengagement of ethylene.

Simultaneous Production of 1 . 6 and 2 . 7-Dimethylanthracenes by the Action of CH_2Cl_2, $CHCl_3$, or of $C_2H_2Br_4$ on Toluene in presence of $AlCl_3$.—James Lavaux.—Already noticed.

Essence of Tetranthera Polyantha, var. Citrate Nees.—Eug. Charabot and G. Laloue.—The analysis of the essence extracted from the leaves of this tree shows that it contains 6 per cent of citral, 21·2 per cent of cineol, and 31·3 of alcoholic principal (geraniol ?). The essence of the bark contains 8 per cent of citral, 20 per cent of citronellal, 56·5 per cent of geraniol, and 2·4 per cent of ethers, while the essence of the fruit consists of 6.4 per cent of citral, 19·4 per cent of geraniol, and 2 per cent of ether.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xli., No. 3, 1908.

Formation of Oxides of Nitrogen in Ozoniser.—W. Manchot.—Ozone prepared from oxygen mixed with nitrogen always contains oxides of nitrogen, but when only small percentages of nitrogen are present the amounts of oxide formed are so small that they cannot be detected unless large volumes of the gas are passed through an absorption agent. The acid properties of ozone are to be ascribed to the presence of oxides of nitrogen, and when the latter are removed the acid reaction also disappears. Thus ozone is not an acid anhydride; its reaction with bases may simply be an addition reaction.

Three Lecture Experiments.—Edmund Knecht.—*Synthesis of Calcium Carbide and Acetylene.*—A piece of calcium as large as a pea is placed upon a hollowed-out piece of coal, and gently heated before the blowpipe. In a few seconds the metal catches fire, and burns with an intense orange-coloured flame, meanwhile sinking into the coal. When the latter is broken, a lump of calcium carbide is found embedded in it. If this is placed in a test-tube and water is added, acetylene is generated. *A Visible Autoxidation.*—A solution of potassium permanganate acidified with sulphuric acid is divided into two parts. One is kept for comparison, and to the other small quantities of titanium sesquisulphate solution are added. The colour of the permanganate solution changes gradually from blue-red to scarlet, and finally the pure orange of titanium superoxide appears. Excess of the reagent decolorises the solution. Titanium sulphate gives

no reaction with permanganate. *Precipitation of Copper as Metal by Titanium Sesquisulphate.* — Commercial titanium sesquisulphate solution is added to a 10 per cent copper sulphate solution, and the whole is well stirred. After a few minutes the metal begins to separate; it appears blue in transmitted light, but the characteristic colour of the metal is seen in incident light. The precipitate is so finely divided that most of it runs through filter-paper. The test is sensitive enough to show the presence of one part of copper in 1,000,000 parts of solution.

Preparation of Bromine Cyanide and Cyanamide Derivatives.—Fritz Baum.—Scholl has shown that when a cold concentrated solution of potassium cyanide is added to some bromine in water, the whole being well cooled, and the crystalline mass obtained is distilled on the water-bath, bromine cyanide distils over. Since, however, the isolation of the cyanide by distillation is a very unpleasant process the author finds that it is preferable to add ether to the crystalline mass, dry the ethereal solution with calcium chloride, and use the bromine cyanide in this form. Such a solution can be directly converted into the corresponding cyanamides by means of methylamine and aniline.

Heat of Formation of Antimony Hydride.—Alfred Stock and Franz Wrede.—The heat of formation of antimony hydride can very easily be determined by measuring the heat evolved when the gas is decomposed by an electric spark. The gas is purified by repeated fractional distillation, and introduced into an exhausted glass tube, which is then fused up. The vessel is placed in a water calorimeter, and a spark is passed by means of platinum wires fused through the glass. The mean of three experiments gave for the heat evolved 34·27 cals. per. grm.-molecule at constant volume, and 33·98 cals. per grm.-molecule at constant pressure, the error being less than 1 per cent. Thus the equation for the formation of antimony hydride at the ordinary temperature is $Sb\,(metal) + 3H = SbH_3 - 33{\cdot}98$ cals. This value does not fit in well with those found for NH_3 (+12·2 cals.), PH_3 (+11·6 cals.), and AsH_3 (−36·7 cals.). Antimony hydride is undoubtedly a more endothermic compound than AsH_3, and probably a fresh determination of the heat of formation of AsH_3 will give a lower value.

Phosphorus Pentasulphide.—Alfred Stock.—The author describes an improved form of apparatus for preparing large quantities of phosphorus pentasulphide, and gives the results of vapour density determinations carried out at different temperatures. These experiments show that the pentasulphide when distilled or sublimed undergoes decomposition, to a slight extent only at atmospheric pressure; in a vacuum or in a current of carbon dioxide the decomposition is more pronounced. Evidently the sulphide with lower melting-point, prepared by Stock and Thiel, consisted of a mixture produced by heating the pentasulphide.

MISCELLANEOUS.

Preparation of Triphenylmethyl.—Julius Schmidlin.—The author describes a convenient apparatus for preparing triphenylmethyl by the decomposition of the magnesium compound of triphenylchlormethane with excess of triphenylchlormethane. A distilling flask is connected with an upright condenser, its side-tube being corked, and in it triphenylchlormethane and iodine are dissolved in absolute ether by gently heating. Then dry magnesium powder is added, and the flask is heated on a water-bath to a temperature just below the boiling-point of ether. After about forty minutes the warming is stopped, and the side-tube of the distilling flask is connected by means of a glass cylinder with the neck of another distilling flask. The glass cylinder is fitted with a filter. The liquid is hen filtered in a current of hydrogen, by inclining the whole apparatus in a vertical plane until the filter is vertical, the second flask being filled meanwhile with coal-gas. When the whole of the liquid has been filtered into the second flask the latter is connected with the condenser and heated on a water-bath until the ether solution begins to boil and triphenylmethyl separates out in colourless crystals. By the use of this apparatus the β-magnesium compound of triphenylchlormethane can be isolated.—*Berichte*, xli., No. 2.

MEETINGS FOR THE WEEK.

MONDAY, 6th.—Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "Considerations affecting the 'Strength' of Wheat Flours," by J. L. Baker and H. F. E. Hulton. "Note on Murexide as a Quondam Dyestuff and Printing Colour," by Watson Smith.
TUESDAY, 7th.—Royal Institution, 3. "The Egyptian Sudan—its History, Monuments, and Peoples, Past and Present," by E. A. Wallis Budge, M.A., &c.
—— Royal Society of Arts, 4.30. "The Imperial Problem of Asiatic Immigration," by Richard Jebb.
WEDNESDAY, 8th.—Royal Society of Arts, 8. "Technical Education in America," by Sir William H. Preece, K.C.B., F.R.S.
THURSDAY, 9th.—Royal Institution, 3. "The Animals of South America," by R. Lydekker, F.R.S.
FRIDAY, 10th.—Royal Institution, 9. "The Carriers of Positive Electricity," by Prof. J. J. Thomson, F.R.S.
—— Physical, 8. "Experimental Investigation of the Nature of the γ-Rays," by W. H. Bragg and J. P. V. Madsen. "Experiments on Artificial Fulgurites," by Miss D. D. Butcher. "Short Spark Phenomena," by W. Duddell.
SATURDAY, 11th.—Royal Institution, 3. "Electric Discharges through Gases," by Prof. J. J. Thomson, F.R.S.

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Municipal Secretary, Singapore.

Municipal Office, Singapore,
February 8th, 1908.

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THE CHEMICAL NEWS.

VOL. XCVII., No. 2524.

"TELLURIUM."

IS IT A MIXTURE OF TWO ELEMENTS?

By WILLIAM BETTEL.

THE following record of a curious experience in the examination of a "telluride" silver ore is now published in order to enlist the interest of chemists, metallurgists, mining engineers, and others engaged in silver mining, with whom the writer has not come into contact (during the past quarter of a century), with a view to the possible discovery of a "telluride" silver ore giving reactions similar to, if not identical with, those obtained in his experiments.

In 1883 the attention of the writer was called to a curious behaviour of silver obtained from assays of a silver "telluride" ore (some three tons of which were under

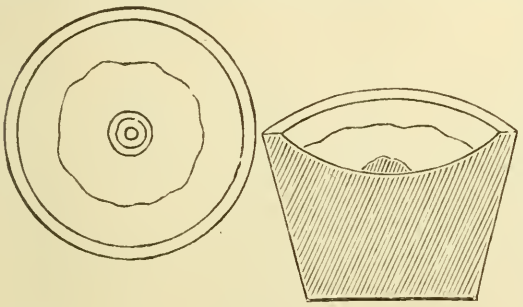


FIG. 1.

offer for sale) at the apparent completion of cupellation. The beads of silver "brightened" and cleared, but, instead of solidifying to buttons in the usual manner, they suddenly lost their surface tension, wetted the cupels as a drop of mercury would wet clean surfaces of zinc, copper, or tin, and spread out in irregular films, leaving a protuberance in the centre of each cupel more or less marked as the bead was exposed for a longer or shorter period to a temperature above that of melting silver, after brightening.

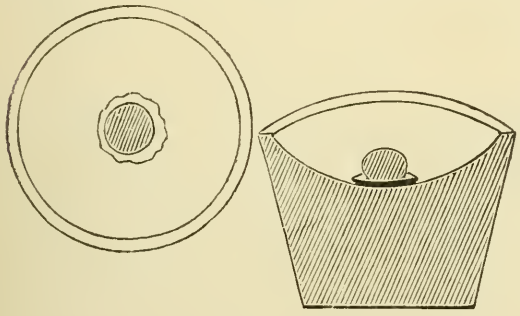


FIG. 2.

In some instances the silver films were over an inch in diameter, the pimple or protuberance being from 2 to 3 mm. diameter by about 1·5 by 2 mm. high, to a "refined" bead, a bead having at its base a ring of silver about 2 mm. width of section, the bead being about 12 to 13 grains in weight (see Figs. 1 and 2).

It was not found possible by the existing methods of potting or scorification, followed by cupellation, to arrive at a satisfactory estimate of the silver contents of the ore, so preliminary treatments were given, having as their object the removal of the tellurium or other constituents which caused the trouble.

Analysis of the ore showed "tellurium" to the extent of 5 to 6 per cent, and the only difference between so-called "chemically pure" tellurium as purchased, and that extracted from the ore, was that the chemically pure element when alloyed with lead and silver left after scorification and cupellation a rim of an average width not exceeding 2 mm., generally 0·5 to 1 mm.

About five pounds of the powdered ore was secured and set aside for further examination as the work in a smelting works and refinery would permit, but stocktaking intervening, a too zealous laboratory attendant consigned this sample to the ore heap, and it was therefore lost. Endeavours were made by the firm, through the sellers, to ascertain the name of the mine, or its locality, without result, as the shippers were merely agents who kept no record of the transaction, and since that period, although the writer has made personal enquiries of a great many English-speaking chemists and metallurgists with whom he has come into contact, not one has had under his observation similar results to those recorded.

Some four years subsequent to these experiences another firm (to which the writer at the time was metallurgist and chemist) purchased the contents of a refinery and smelting establishment which had, it appears, purchased the refractory telluride silver ore, but only small quantities of the element, which the writer ventures to call (provisionally) "β-tellurium" were observed. It was present (in traces) in the otherwise fine silver, also in larger amounts in slags, skimmings, flue dust, stained surfaces of firebrick ("cobbing"), argentiferous copper-matte, and litharge (all of which were purchased). The maximum width of ribbon or fringe round the silver beads did not measure in any case more than 2 mm., generally from 0·5 to 1 mm., about the same as is noticed in cupelling ordinary silver-lead to which has been added so-called pure tellurium.

The element present in the originally examined ore possessed the following properties (in combination with silver):—

1. It formed a true chemical compound with silver less easily oxidisable than lead, bismuth, tellurium, selenium, antimony, &c.

2. It prevented the absorption of oxygen by silver at the close of the cupellation.

3. It was not finally removed by repeated cupellation with lead or bismuth, even after allowing the silver bead in which it was contained to remain fluid long after "finishing" as ordinarily understood.

4. It was soluble in sulphuric acid, and imparted the same tint to that acid as is produced by ordinary tellurium.

5. Its other chemical reactions called for no specia notice, the substance being estimated as "tellurium."

6. Distinct amounts of this substance have been found in all "tellurium" samples examined (by testing its action on silver in cupellation) by the writer.

7. The present accepted atomic weight of tellurium (127·6) places it in an anomalous position in regard to other elements in the periodic system. In "Select Methods in Chemical Analysis," 1905, p. 420, is the following:—

"On account of the fact that the most trustworthy determinations of tellurium have given results which place it in the eighth group of the periodic system of the elements, notwithstanding its striking similarity to sulphur and selenium, the hypothesis has been put forward that tellurium is a mixture of true tellurium with an atomic weight of about 125 and another element with a higher atomic weight.

"Brauner (*Journ. Chem. Soc.*, lxv., 382, and lxvii., 549), who spent a number of years studying tellurium, has expressed this as his opinion."

8. No known substance produces the effects in cupellation of silver as were witnessed in the experiments with

the "telluride" ore in 1883, nor has any substance other than the "tellurium" of commerce yielded results which approximate in any degree to those of the experiments in 1887.

9. The silver film and protuberance previously referred to in the description of the 1883 experiments, when freed from litharge and cupel matter, dissolved completely in nitric acid, and also in sulphuric acid, in both of which the "β-tellurium" was presumably oxidised.

As desultory enquiries during twenty-five years have yielded no results, it is now time to apply to a wider circle, and by the kind consent of the Editor, to whom the writer (in Johannesburg in 1896) detailed his experiences in this direction, an appeal is made to all interested in deposits of "telluride" silver ores to submit samples to the writer for examination. Should any be found giving the same reaction as has been here described, and presumably containing the long-looked-for new element, they will be forwarded to Sir William Crookes for his opinion.

Chemical and Metallurgical Laboratories,
379, Commissioner Street,
Johannesburg, Transvaal, South Africa.

[We wish to draw the attention of our readers to the request made by Mr. Bettel in the above paper. It has long been surmised that tellurium is accompanied by another element of a different atomic weight, but this is, we believe, the first hint given by chemistry that such an element may really exist. Mr. Bettel writes saying he will be very pleased to receive and examine specimens of silver telluride ores which have been found difficult to assay by the usual process, and if full particulars regarding locality of the ore deposit, name of mine and sender, with address of the latter, be attached, he will forward to the Editor of this journal any sample which he considers may contain the sought-for element.

We shall be glad if editors of mining, metallurgical, and technical papers will copy Mr. Bettel's article and this Editorial Note in order to secure greater publicity by circulating the information among mining men, and others who are not chemists but are interested in silver mining and reduction works, in Mexico and elsewhere.—*Ed.* C. N.]

THE CONVERSION OF DIAMOND INTO COKE IN HIGH VACUUM BY CATHODE RAYS.*

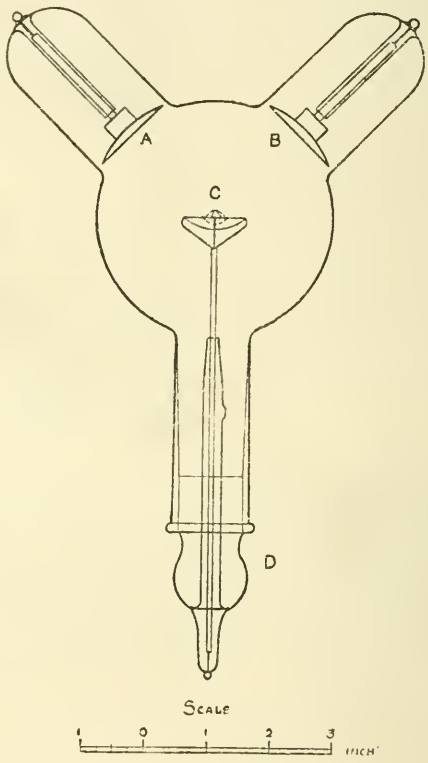
By the Hon. CHARLES A. PARSONS, C.B., F.R.S.,
and
ALAN A. CAMPBELL SWINTON.

The objects of the experiment were three-fold: firstly, to ascertain whether a diamond could be entirely converted into coke or graphite by heating in a vacuum by cathode rays; secondly, in the event of this being found practicable, to make a determination by Féry's optical pyrometer of the temperature at which the conversion takes place; thirdly, to endeavour to ascertain if, during the conversion, any gas was emitted or absorbed by the carbon.

The vacuum tube employed is shown in the illustration, where A and B are the two aluminium electrodes, C the diamond, and D an air-tight ground-glass stopper joint, through which the diamonds were introduced. Alternating current was employed, each of A and B acting as cathode and anode in turn, while their concave curvature was such as to accurately focus the cathode rays on to the diamond. The latter was supported on a plate of iridium, which, in turn, rested in a platinum cup, this arrangement being designed to prevent any stray cathode rays which might miss the diamond from striking the glass walls of the tube and melting the latter. During the experiment the tube was connected to two mercury pumps of the Toepler type, and in connection with the tube there were also attached two spectrum analysis discharge tubes for the purpose of collecting and examining some of the residual gas in the tube, both before and after the conversion of the diamond into coke.

The alternating current from the mains, which was of 85 periods per second, was passed through the primary of a 10-inch Rhumkorff coil, with the contact-breaker and condenser disconnected, with an adjustable choking coil in series in the primary circuit, so that the secondary voltage could be varied from about 5000 to 12,000 volts. A reflecting milliampère-meter was employed to read the current through the tube, while the volts across the tube's terminals were measured by an electrostatic voltmeter.

The two diamonds, each about 0·2 inch in diameter, were experimented with. The first was entirely converted into coke without difficulty, while in the case of the second



the process was stopped when most of it had been so converted, the residue being black throughout its mass. As the proper degree of vacuum was reached by working the mercury pumps, and as the volts were raised, the diamond in each case became red, and then intensely white-hot, till, with about 8000 volts and 44 milliampères (352 watts) passing through the tube, the diamond began to throw off small sparks. On the volts being increased to 9600, and the current rising to 45·5 milliampères (436 watts), the sparks thrown off became more numerous and the diamond commenced to become black. Finally, with 11,200 volts and 48 milliampères (537 watts), a rapid disintegration of the diamond took place, with considerable increase in volume, the residue having much the appearance and consistency of coke.

The temperature of the diamond, as given by the pyrometer during disintegration, was 1890° C.

During the heating up of the diamond and of the tube, large amounts of gas were driven off, and had to be pumped out, but there was nothing to indicate that any

* A Paper read before the Royal Society, January 16, 1908. From the *Proceedings of the Royal Society*, A, vol. lxxx., p. 184.

of this gas originated from the diamond rather than from the metal parts and glass walls of the tube. Two experiments were made, and in the latter there was distinct indication of a rise in vacuum just about the time of the conversion. These rises in vacuum are, however, not unusual in tubes in which there is highly heated metal, and it was impossible to decide whether any of the absorption of gas took place in the diamond.

In the experiment in question, one of the spectrum discharge tubes was sealed off just before the conversion, when the diamond was commencing to blacken on the surface, while the other was sealed off after the diamond had been converted into coke. These two tubes, therefore, respectively contained samples of the residual gas before and after the conversion. Their spectra have been photographed alongside of one another, but though they are not altogether the same, the differences do not appear sufficiently marked to determine with exactitude any variation in the nature of the gases present.

The experiments were arranged and carried out by Mr. Swinton at his laboratory in London.

THE HISTORY OF VALENCY.

By J. NEWTON FRIEND, Ph.D., M.Sc.

The Origin of the Theory.

It seems at first sight rather remarkable that the enunciation of Dalton's law of multiple proportions did not at once lead chemists to a conception of valency. Although it was now known that compounds were formed by the union of atoms of different elements, the idea that the individual atoms possessed a definite attractive force was not for many years entertained. In fact, forty-four years elapsed between the publication of Dalton's famous book in 1808, entitled "A New System of Chemical Philosophy," and Frankland's discovery of that atomic force, known to-day as valency, which was announced in 1852 in the *Philosophical Transactions*. In 1858 two papers appeared simultaneously, one by Couper (*Ann. Chim. Phys.*, [3], liii., 469; *Comptes Rendus*, xlvi., 1157), the other by Kekulé (*Ann.*, cvi., 129) in which Frankland's views were enlarged.

Couper rejected the type theory entirely, and constructed formulæ for various compounds by applying his knowledge of the valencies of the constituent atoms. Had he employed the same atomic weights as we to-day his formulæ would in many cases have been identical with those still in vogue.

Kekulé, on the other hand, was impregnated with the type theory, and endeavoured to harmonise the new views with the old.

Variability of Valency.

The early development of the theory of valency was beset with difficulty. It is true that hydrogen forms an excellent standard, in that its atom is never known to combine with more than one atom of any other element. The numerical value of its valency may therefore be taken as unity, and by analysing its hydrides the valency of any other element could be determined. But not only was this method soon found to be unsatisfactory on account of the paucity and instability of the metallic hydrides known, but the method yielded contradictory results.

Thus, writing the formula for hydrochloric acid as H.Cl, it is clear that the valency of chlorine can only be unity. But two chlorides of phosphorus are known, namely, the trichloride, PCl_3, and pentachloride, PCl_5, in which the valency of phosphorus is 3 and 5 respectively.

It is obvious, therefore, that if the above reasoning is valid, valency cannot be regarded as a constant quantity.

Both Frankland and Kolbe were of this opinion. Kekulé, on the other hand, preferred to regard valency as a fundamental property of the atom, and as unchangeable and invariable as the atomic weight—a view which he retained to the last (*Zeit. Chem.*, vii., 689).

In order to explain the formation of phosphorus pentachloride, Kekulé argued that it was a molecular compound, and that its formula would be more correctly written as $PCl_3.Cl_2$.

The fact that this substance dissociates on vaporisation was taken as supporting this view.

A similar explanation was applied in the case of ammonium chloride, $H_3N.HCl$.

During the past few years, however, a large number of facts has been been accumulated which cannot be reconciled with Kekulé's doctrine of constant valency. The discovery of phosphorus pentafluoride, PF_5, which can exist in the gaseous state without dissociation, definitely proves the pentavalence of phosphorus (Thorpe, *Ann.*, 1876, clxxxii., 201).

The remarkable researches of Baker have further established the pentavalence of nitrogen, by showing that perfectly dry ammonium chloride may be vaporised without dissociation (*Trans. Chem. Soc.*, 1894, lxv., 612).

In nitric oxide, NO, nitrogen is apparently divalent, for the molecules of this gas have been proved to be single, even at $-100°$ C.

Kolbe ("Lehrb. d. Anorg. Chem.," 1856, i.) believed that each element possessed a definite maximum valency, and when this was saturated, further combination became impossible. Erlenmeyer, some years later, adopted a similar view (*Zeit. Chem.*, 1863, pp. 65, 97, 609; 1864, pp. 1, 72, 628).

Mendeleeff assumed that the highest oxygen compounds, omitting peroxides, give the maximum valency of the elements (Ostwald's "Klassiker," lxviii., 48), and Abegg has adopted the same suggestion (*Zeit. Anorg. Chem.*, 1904, xxxix., 340).

Not only is this method uncertain, owing to the divalent nature of oxygen, but it is inconsistent. The valency of manganese, for example, is decided by a much higher and more unstable oxide (Mn_2O_7) than the peroxide (MnO_2) (compare Friend, *Trans. Chem. Soc.*, 1908, xciii., 262).

Abegg further suggests that the maximum valency of every element is 8, and apparently Morozoff is of the same opinion (*Journ. Russ. Phys. Chem. Soc.*, 1906, xxxviii., [2], 481).

Although this is true for the majority of the amphoteric elements, it can scarcely be so in the case of the inert gases, hydrogen, and the alkali metals.

Up to the present no satisfactory theory has been advanced to account for the variability of valency. Abegg assumes that all the valencies of an atom are of the same strength before actual combination, but saturation of one weakens the rest. The extent of that weakening determines the numerical value of the valency in the circumstances (see Abegg and Bodländer, *Zeit. Anorg. Chem.*, 1899, xx., 453).

Nef, on the other hand, believes that the unused valencies do not lie latent in the ordinary sense of the term. They saturate one another. He therefore writes Cl≡Cl for the molecule of chlorine, R—Cl⊐ for alkyl chlorides, and $H_3N\sqsupset$ for ammonia (*Ann.*, 1897, ccxcviii., 202). This theory offers no explanation for the existence of *one* unsaturated valence such as occurs, for example, in cuprous chloride, CuCl. This difficulty was overcome by doubling the formula, a procedure which was apparently justified by the results of vapour density determinations effected by Biltz and V. Meyer (*Ber.*, 1889, xxii., 725), and V. Meyer and C. Meyer (*Ber.*, 1879, xii., 609, 1112, 1185, and 1292).

In 1897, however, Werner (*Zeit. Anorg. Chem.*, xv., 565) showed that in solutions of pyridine, cuprous chloride consists of single molecules. Rügheimer and Rudolphi (*Ann.*, 1905, cccxxxix., 311) have shown that the same is true for solutions in fused bismuth chloride, and E. Beckmann and Gabel have obtained similar results in a series of experiments carried out with quinoline as solvent (*Zeit. Anorg. Chem.*, 1906, li., 236). Copper must there-

fore be regarded as truly monovalent in cuprous salts, one valence remaining inactive. Other metals have been found to offer similar difficulties, and no explanation is as yet forthcoming.

The Valency of Carbon.

The determination of the numerical value of the valency of carbon was an important advance in the theory of valency, and one destined to exert an enormous influence on the study and progress of organic chemistry.

In 1854, Williamson and Kay prepared tri-ethyl ortho-formate—

$$C\begin{cases} H \\ (OC_2H_5)_3 \end{cases}$$

by the action of chloroform on sodium ethoxide,—

$$CHCl_3 + 3NaOC_2H_5 = 3NaCl + CH(OC_2H_5)_3.$$

They described it as "a body in which the hydrogen of three atoms of alcohol is replaced by the tri-basic radical of chloroform" (*Proc. Roy. Soc.*, vii., 135). In the light of our present knowledge it seems most remarkable that these investigators did not at once realise the tetravalency of carbon. This, however, was seemingly reserved for Kekulé.

In a paper on the constitution of fulminic acid (*Ann.*, 1857, ci., 200) Kekulé drew up a table of the compounds belonging to the marsh-gas type. Thus :—

C_2 H H H H	Marsh-gas.
C_2 H Cl Cl Cl	Chloroform.
$C_2(NO_4)Hg$ $Hg(C_2N)$	Mercuric fulminate.

It is clear from this table that Kekulé regarded C_2 as tetravalent, where by C_2 he understood C, the symbol used by the Gerhardt-Williamson school to denote the atom C = 12.

In a paper published later in the same year (*Ann.*, 1857, civ., 129), he distinctly states in a foot-note (p. 133) that he regards one atom of C = 12 as equivalent to four atoms of hydrogen.

The valency of carbon has proved to be remarkably constant, and it is largely due to this property that the application of the theory of valency to the study of organic chemistry has met with such success. Until quite recently carbon was believed to be divalent in carbon monoxide, C = O. The discovery of Collie and Tickle (*Trans. Chem. Soc.*, 1899, lxxv., 90), that oxygen can function as a tetravalent atom, renders this assumption doubtful. Nevertheless, Nef (*Journ. Am. Chem. Soc.*, 1904, xxvi., 1549) prefers to write divalent carbon in carbon monoxide, hydrocyanic acid, H—N = C, &c.

In triphenyl methyl, $C(C_6H_5)_3$, carbon appears at the first blush to function as a trivalent element (Gomberg, *Ber.*, 1900, xxxiii., 3150), but the question is by no means settled, several other formulæ having been suggested. It may therefore be safely asserted that up to the present no compound has been prepared in which carbon functions other than as a tetravalent atom.

Thiele's Theory.

Thiele studied compounds of the type—

$$\begin{matrix} R_1 \\ R_2 \end{matrix}\!\!>\!C=CH-CH=C\!<\!\!\begin{matrix} R_3 \\ R_4 \end{matrix},$$

and concluded that the double bonds do not represent a complete saturation of the atoms, but that each atom possesses a "partial" valency in addition. In this way he finds an explanation for the fact that bromination of such a group gives a double bond in the middle. Thus,—

$$\begin{matrix} R \\ R \end{matrix}\!\!>\!CBr-CH=CH-CBr\!<\!\!\begin{matrix} R \\ R \end{matrix}.$$

In order to represent this partial valency, Thiele proposes the use of dotted lines. Thus, for carbon monoxide he writes $\overset{\vdots}{C}=\overset{\vdots}{O}$, $\overset{\vdots}{N}=\overset{\vdots}{N}$ for nitrogen, &c. Thiele has further extended his theory to the study of the benzene nucleus and aromatic compounds generally (*Ann.*, 1899, cccvi., 87; cccviii., 213).

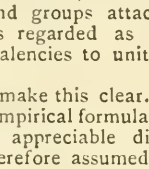
Following along somewhat similar lines, Baeyer was led to advance his theory of "complex valency" (*Ber.*, 1901, xxxiv., 2685), and Bulow a theory of "crypto valency" (*Ber.*, 1901, xxxiv., 3920).

Werner's Theory.

After a careful study of the complex ammino compounds, Werner was led to suggest a new theory of valency, by means of which he was able to group these substances in well defined classes.

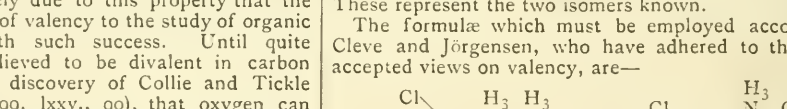
It is impossible to do full justice to his ingenious theory in the limited space at our command, but the student will find a very clear exposition of the same in Werner's book, entitled "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 1905. Werner distinguishes two kinds of valency, known as Principal and Auxiliary. The former correspond to the generally accepted valencies of the elements. The latter, however, possess a smaller energy content, and groups attached by them are not dissociable. It is regarded as possible, however, for several auxiliary valencies to unite to form a principal valence.

An example will make this clear. Two compounds are known having the empirical formula $PtCl_4(NH_3)_2$. Neither isomer shows any appreciable dissociation in aqueous solution. It is therefore assumed that the six elements or groups are attached directly to the platinum, the four chlorine atoms by principal valencies, and the two NH_3 groups by auxiliary. Thus—



It is clear that if the groups are arranged spatially around the platinum atom two different schemes are possible, namely, one in which the two NH_3 groups are adjacent, and one in which they are opposite to one another. These represent the two isomers known.

The formulæ which must be employed according to Cleve and Jörgensen, who have adhered to the usually accepted views on valency, are—



These formulæ are not only clumsy, but fail to explain the undissociable nature of the complexes.

Electro-chemical Theories.

The theories which, up to the present, have engaged our attention, have assumed that valency is merely an attractive force. The most casual observer, however, cannot fail to be struck by the fact that the most stable compounds are formed by the union of elements of opposite electrical character. It is not remarkable, therefore, that numerous attempts should have been made from time to time to account for chemical combination on electro-chemical grounds.

The Dualistic Theory of Berzelius was essentially electro-chemical, and even in 1869 Blomstrand made the interesting observation that an element which is decidedly electropositive or negative has the lowest saturation capacity. Thus, if the halogens act decidedly negatively their valency is always unity (*Chemie der Jetztzeit*, 1869, 217, 243).

In 1899, Abegg and Bodländer (*Zeit. Anorg. Chem.*, xx., 453; see also Abegg, *Ibid*, 1904, xxxix., 331) discussed an electrochemical theory of valency in full, but it presented several difficulties and has not been generally accepted.

In 1902, Spiegel suggested that certain elements possess what he calls *neutral affinity*, that is, valencies which can

be called out in pairs of equal opposite sign, and which when not externally saturated, neutralise one another. They exert, therefore, no action on the electrochemical character of the element (*Zeit. Anorg. Chem.*, 1902, xxix., 365).

Arrhenius ("Theorien der Chemie," 1906) has given expression to somewhat similar views. Neither author has, however, worked out the subject with any degree of fulness.

Friend (*Trans. Chem. Soc.*, 1908, xciii., 260) distinguishes three kinds of valency, namely :—

1. *Free Positive Valency*, such as that possessed by hydrogen and the metals. Its numerical value for any particular element is determined by analysis of the fluorides.

2. *Free Negative Valency*, such as that possessed by fluorine and chlorine. Its numerical value in any particular case is determined by analysis of the hydrides. All the non-metals, with the exception of the two already mentioned, possess free positive valency in addition to negative. They are therefore termed *amphoteric* elements.

3. *Latent* or *Residual Valencies*.—These are possessed by every element, not excepting the inert gases. They are called out in pairs of equal and opposite sign, and in this respect resemble those of Spiegel and Arrhenius. It is assumed that in all cases latent and free valencies possess the same chemical nature, and in support of this the work of Victor Meyer on the alkyl ammonium iodides is cited.

No theory may be regarded as final. But let not the investigator be discouraged. Each new thought, even if it be wide from the mark, serves to stimulate us to further research, and to promote the interests of science and truth.

DETERMINATION OF THE ATOMIC WEIGHT OF EUROPIUM.

By G. JANTSCH.

DETERMINATIONS of the atomic weight of europium have been published in three articles. E. Demarçay (*Comptes Rendus*, 1900, cxxx., 1469) gave the value Eu = 151. This is certainly too low, and it is probable that his earth contained samarium, or that his measurements were incorrect. G. Urbain and H. Lacombe (*Comptes Rendus*, 1904, cxxxviii., 627) published a series of determinations of the successive members of a fractionation by which they obtained spectroscopically pure europium. These determinations were performed chiefly in order that there might be no doubt about the constancy of the atomic weights and the homogeneity of the europium. The method consisted in transforming the octohydrated sulphate into anhydrous sulphate, and the numbers thus obtained were verified by converting the anhydrous sulphate into oxide. The mean of the values obtained (adopting the international atomic weights, O = 16) was Eu = 151·99. More recently. W. Feit and Przibylla (*Zeit. Anorg. Chem.*, 1906, l., 248) have performed fresh determinations with a europium prepared by Urbain. Their method consisted in dissolving the ignited oxide in a known volume of titrated sulphuric acid, and determining volumetrically the excess of acid. Thus they found Eu = 152·57.

A new determination was necessary owing to the differences between these results. I am indebted to M. Urbain for some europium which he kindly gave me for this purpose.

In order to convince myself that this earth was pure, I photographed on the same plate, one above the other, the spectra of gadolinium, europium, and samarium in the order specified. The spectrum of iron was used as a reference spectrum. These spectra were obtained by the electric arc, following the directions recently published by Griner and Urbain (*Bull. Soc. Chim.*, 1907 [4], i., 1158). It was shown that none of the gadolinium lines, nor those of samarium, were prolonged into the europium spectrum. The only lines common to the three spectra were the parasitic lines of the arc, appearing owing to the presence of a small amount of iron, silicon, and magnesium in the carbon electrodes.

As there was no doubt about the purity of the material, my attention was concentrated on perfecting the experimental details of the determination. For this purpose I studied specially the method which has been devised by Urbain and Lacombe.

I proceeded as follows :—

About 1·2 grms. of oxide were converted into neutral nitrate. To the solution of this nitrate (amounting to about 10 cc.) a slight excess of pure sulphuric acid was added, and the whole was poured into a large volume (about 1 litre) of alcohol at 95°. Under these conditions the transformation of the europium nitrate into octohydrated sulphate has been found to be complete. The sulphate appears as a precipitate formed of fine crystalline silver-white needles. This precipitate was then washed with alcohol until all the sulphuric and nitric acids were eliminated, and dried in an air-oven at 300° to transform it into anhydrous sulphate. The sulphate was dissolved in the least possible quantity of water, and the perfectly neutral solution was evaporated very slowly in an air-oven, kept nearly closed, at a constant temperature of 105°. The crystals were deposited on the walls of the vessel. Those which formed on the sides, and which had thus not been constantly washed with the mother-liquor, were rejected. Only those crystals which were deposited on the bottom of the vessel were used for the determinations. These crystals were powdered and dried over sulphuric acid. The drying took two or three days.

Under these conditions the octohydrated sulphate loses all water of interposition, but no water of crystallisation. The salt was weighed in a tared platinum dish. I had found that when this dish was heated to 1600° it suffered absolutely no loss of weight. The weighed sulphate was first dried in an air-oven in a double platinum crucible. The temperature was slowly raised to 325°. The drying was completed by maintaining this temperature for an hour. Then the crucible, without being cooled, was introduced into a little gas furnace, inside another platinum dish. The temperature of the furnace was raised to a white heat, and maintained for one hour. Then the crucible was allowed to cool in a phosphoric anhydride desiccator for ten minutes only, in order to avoid absorption of dry gases by leaving it too long. This absorption is very slight, but it falsifies any correction of weight for the pressure of the air.

The crucible was then weighed and heated a second time. There was generally no change in the second weighing.

In order to prove that the oxide retained no trace of sulphur, one part of the oxides was fused with a mixture of pure sodium carbonate and sodium nitrate. When the fused mass was taken up with water no sulphuric acid was ever detected in the filtered liquid.

The weighings were performed with a Curie's aperiodic balance, sensitive to one-tenth of a mgrm.

The initial and final states of the transformation being perfectly definite, and the method being affected by no causes of loss, the results can be affected only by accidental errors. The exiquity of these can be seen from the following table :—

O = 16, H = 1·008, S = 32·06.

Weight of sulphate, $Eu_2SO_4\,8H_2O$.	Weight of oxide, Eu_2O_3.	Atomic weight.
1·3501	0·6455	152·032
1·5054	0·7197	152·009
1·5213	0·7274	152·054
1·2881	0·6159	152·056

The mean value is 152·03, with an error $\pm$ 0·02

These numbers agree with those obtained by Urbain and Lacombe.—*Comptes Rendus.*, 1908, cxlvi., 473.

SELENIUM NITRIDE.

By VICTOR LENHER and E. WOLESENSKY.

When ammonia gas is brought in contact with selenyl chloride in the cold, the reaction, according to Michaelis (*Jeanische Zeit.*, vi., 91), proceeds as follows: $6SeOCl_2 + 16NH_3 = 3SeO_2 + 3Se + 4N + 12NH_4Cl$. Michaelis in studying this reaction, brought ammonia gas directly in contact with selenyl chloride. At low temperatures only slight action was noted, while at higher temperatures, the reaction proceeds with evolution of heat.

In studying the behaviour of ammonia gas when conducted into a solution of selenyl chloride in either benzene or oluene, the reaction under these conditions was found to be of a different character than that indicated by the equation of Michaelis, one of the principal products being the nitride of selenium.

When dry ammonia gas is conducted into a strong solution of selenyl chloride in benzene or toluene, considerable heat is evolved and a brick-red precipitate forms, which, when treated with cold water, leaves a bright red residue. This residue when dissolved in nitric acid shows complete absence of chlorine, but a large percentage of selenium.

Quantitative data obtained on the precipitate obtained before treatment with water seem to indicate that it consists of ammonium chloride, selenium, selenium dioxide, and a small amount of selenium nitride.

By using a more dilute solution of selenyl chloride (2 to 4 per cent) in benzene, the reaction is materially moderated, and a buff-coloured precipitate appears, which on drying becomes orange-red. This material, when washed with cold water to remove the ammonium salts, and then extracted with potassium cyanide to remove the free selenium, left a brick-red nitride, which proved to be a highly explosive body. Analyses showed:—

	I.	II.	Calculated for SeN.
Se	84·7	84·7	84·8
N	15·5	16·3	15·2

Espenscheid (*Ann. Chem.*, cxiv., 101) obtained this compound by conducting dry ammonia gas diluted with hydrogen over selenium tetrachloride cooled by a freezing mixture, and obtained a brown mass which, when treated with water and extracted with carbon bisulphide or potassium cyanide, left an orange red powder of SeN, which exploded violently when struck or when brought in contact with chlorine or hydrochloric acid either in the gaseous form or in concentrated solution. When heated to 150° it began to darken, and exploded at 200°. On the other hand, the nitride obtained by the action of ammonia on selenyl chloride dissolved in benzene begins to darken at a comparatively low temperature, and explodes at 130°. When the substance has been carefully purified and is thoroughly dry a slight shock will cause it to detonate violently.

Verneuil, in a manner differing but slightly from that of Espenscheid, obtained a similar substance, but to which he ascribed the formula Se_3N.

The result of the interaction between ammonia and selenyl chloride in benzene solution evidently depends on the temperature and the concentration of the reacting substances. When the temperature is not too high and the solution is dilute, a highly explosive compound of selenium and nitrogen is formed which has the composition SeN. If, however, a solution of considerable strength be employed, the temperature of the reaction causes the separation of a large quantity of free selenium.—*Journal of the American Chemical Society*, xxix., No. 1.

Phosphorus Oxybromide.—E. Berger.—Phosphorus oxybromide can be prepared by mixing the pentabromide and phosphoric anhydride, and heating the mixture until bromine begins to be evolved. The mass then gradually liquefies, and at the end of the reaction it is distilled. The yield is 85 per cent, the equation being $3PBr_5 + P_2O_5 = 5POBr_3$. The oxybromide fuses at 55—56°, and boils at 189·5° under 774 mm. pressure. Its vapour density is normal.—*Comptes Rendus*, cxlvi., No. 8.

THE IODOMETRIC DETERMINATION OF COPPER.*

By F. A. GOOCH and F. H. HEATH.

When potassium iodide is added to a suitable solution of a cupric salt, cuprous iodide is precipitated while iodine equivalent to the amount of iodine fixed in the cuprous iodide is liberated. This reaction has been made the basis of an iodometric method for the determination of copper. The first suggestion of such a method appears to have been made by De Haen in 1854. In this process cupric sulphate was treated in solution with potassium iodide and the free iodine determined by sulphurous acid according to Bunsen. From the amount of iodine thus found the copper was calculated, according to the equation $2CuSO_4 + 4KI \rightarrow 2K_2SO_4 + Cu_2I_2 + I_2$.

This method was mentioned in the following year by Mohr ("Titrirmethode," p. 387), with the modification suggested by Schwarz that the free iodine be determined by sodium thiosulphate instead of by sulphurous acid. E. O. Brown (*Journ. Chem. Soc.*, x., 65), apparently without knowledge of De Haen's previous work, proposed, in 1857, similar procedure, and in 1868 the method with slight modification was presented again by Rümpler (*Journ. Prakt. Chem.*, cv., 193). Concerning the utility of the method opinions have varied. Mohr never favoured it. So late as 1877 Mohr ("Titrirmethode," 5 Aufl., 288), after quoting Meidinger to the effect that cuprous iodide freshly precipitated and washed is capable of taking up iodine, and Carl Mohr's criticism that potassium iodide acts upon cuprous iodide according to the concentration, states that the method is not exact and has nowhere found practical application. On the other hand, Fresenius ("Quant. Anal," 1875, 6te Aufl., 335) recommended the method for the determination of small amounts of copper, noting that ferric salts and other substances capable of setting free iodine from an acidified solution of potassium iodide must not be present, and indicated the most favourable procedure. The copper salt treated, he says, should be the sulphate, preferably in neutral solution, though a moderate amount of sulphuric acid is not objectionable. Much free sulphuric acid and any free nitric acid should be neutralised by sodium carbonate, and the precipitate dissolved in acetic acid, an excess of which does no harm in the iodometric process.

Of recent writers some have favoured the method while others have commented upon it unfavourably. Low (*Journ. Am. Chem. Soc.*, xviii., 468; xxiv., 1083) has been outspoken in praise, to the extent of declaring a preference for this method in the most accurate technical work over all other methods, even the electrolytic method.

According to Low's earlier modification, metallic copper is dissolved in nitric acid, the solution is freed from nitrogen oxides by boiling, a considerable amount of zinc acetate is added, and in the solution having a volume of 50 cc. an excess of solid potassium iodide is dissolved. Zinc acetate is preferred to sodium acetate to take up the free nitric acid. It is said that an excess of potassium iodide is necessary to insure rapidity of action and is harmless. According to the later modification of this method Low prepares the cupric salt by dissolving the metal in nitric acid (sp. gr. about 1·20), boils the solution, adds bromine water to destroy the nitrogen oxides, boils to expel the bromine, treats with ammonium hydroxide in excess, adds acetic acid, and boils again if necessary to get a clear solution. The advantage of using an excess of potassium iodide is emphasised, and the statement is made that unless an excess of this reagent is present the reaction does not proceed to completion until the titration of the free iodine takes place. Low recommends the use of 1 grm. of potassium iodide, an excess of 0·6 grm., for every 0·075 grm. of copper.

Various criticisms have also been made of the reaction

* From the *American Journal of Science*, [4], xxiv., p. 65.

when employed in gravimetric estimations of the cuprous iodide precipitated. Pisani (*Comptes Rendus*, xlvii., 294) notes that potassium iodide can be used to effect the precipitation of cuprous iodide, and that satisfactory separations may thus be brought about.

Flajolot (*Journ. Prakt. Chem.*, xi., 105) states that potassium iodide cannot be used as the precipitant since it dissolves cuprous iodide, and recommends the precipitation of cuprous iodide from the solution of copper sulphate slightly acidified with sulphuric acid, by treatment with sulphurous acid and hydriodic acid. Kohner (*Zeit. Anal. Chem.*, xxvii., 213) affirms that cuprous iodide is soluble both in hydriodic acid and in potassium iodide.

Browning (*Am. Journ. Sci.*, 1893, [4], xlvi., 280) has shown that cuprous iodide may be satisfactorily precipitated and separated from a cadmium salt by adding to a solution of cupric sulphate a moderate excess of potassium iodide (1 grm. to 4 grms. in all), expelling iodine and hydriodic acid by evaporating the solution to dryness, and treating the residue with water, filtering off the precipitate, and weighing upon asbestos in the perforated crucible.

As a result of elaborate study Moser (*Zeit. Anal. Chem.*, 1904, xliii., 597) has reached the conclusion that the reaction by which cuprous iodide is formed from potassium iodide and cupric sulphate in neutral solution is complete at very high concentration of the solution; that the completeness of the reaction is greatly affected by the volume of liquid; that the amount of potassium iodide employed is almost without influence either in neutral solution or in acid solution; and that the presence of free sulphuric acid even in large amounts or of hydrochloric acid present in amount equivalent to the cupric sulphate is advantageous. Moser recommends, therefore, the addition of sulphuric acid for the purpose of bringing the reaction to completion. To the cupric sulphate (about 0·6 grm.) dissolved in 50 cc. of water contained in a 300 cc. stoppered flask are added 5 cc. of 10N/1 H_2SO_4, and 2 grms. of solid potassium iodide; the mixture is shaken frequently for two minutes, and the free iodine is titrated by sodium thiosulphate, with stirring, to the end-reaction of the starch indicator.

According to Fernekes and Koch (*Journ. Am. Chem. Soc.*, xxvii., 1229), an excess of acetic acid does not influence titrations, while a certain amount of potassium iodide—1·5 to 2 grms. for 0·0038 grm. of copper, and 2·5 grms. for 0·0939 grm. of copper—must be added to bring about complete action in a volume of 100 cc.

Quite recently Cantoni and Rosenstein have tested the reaction between potassium iodide and a cupric salt under various conditions (*Bull. Soc. Chim.*, 1906, [3], xxxv., 1067); but these investigators do not give the absolute values of the amounts of copper taken and found, merely recording the relative effects of varying conditions. From the record of their results it would appear that a fivefold increase of the minimum amount of potassium iodide added to portions of 100 cc. of solution containing the same amount of copper salt is without influence upon the result; that increase of volume from 100 cc. to 350 cc., other conditions being the same, may affect the results by as much as 5 per cent of their value. The authors conclude that the method gives good results under properly controlled conditions.

So evidence and opinions as to the effects of various conditions in the process are contradictory.

The chief matters of difference concern the influence of an excess of potassium iodide used as the precipitant, the dilution at which the precipitation should take place, and the effects of acids upon the formation of the cuprous iodide. We have thought it desirable, therefore, to again study these points experimentally.

In the experiments detailed in Table I., small amounts of a solution of pure copper sulphate, standardised by the electrolytic method and containing 0·0020 grm. to 1 cc., were drawn from a burette and treated with potassium iodide in solution. In some of the experiments the iodine set free was titrated without previous dilution, while in others the mixture was diluted previous to the titration. The volumes at precipitation and at the end of the titration are noted. In Series A is shown the effect of twice the amount of potassium iodide theoretically required, at volumes varying from 30 cc. to 80 cc. at precipitation and from 36 cc. to 86 cc. at the end of the titration.

In the experiments of Series B the effect of increasing the amount of potassium iodide under conditions otherwise similar is studied. In Series C is shown the effect of large dilution of the solution containing the amount of potassium iodide used in the experiments of Series A.

Table I.—*Effects of Volume of Solution and Concentration of Potassium Iodide.*

Copper taken as $CuSO_4$.	Volume at precipitation.	Volume at end of titration.	KI used.	Copper equivalent to I found by $Na_2S_2O_3$.	Error in terms of copper.
Grm.	Cc.	Cc.	Grms.	Grm.	Grm.
			A.		
0·0400	30	36	0·4	0·0391	−0·0009
0·0400	40	46	0·4	0·0387	−0·0013
0·0400	50	56	0·4	0·0388	−0·0012
0·0400	60	66	0·4	0·0391	−0·0009
0·0400	80	86	0·4	0·0391	−0·0009 (*a*)
			B.		
0·0400	40	46	0·8	0·0400	—
0·0400	30	36	8·0	0·0399	−0·0001 (*b*)
0·0400	45	54	13·0	0·0599	−0·0001 (*b*)
			C.		
0·0400	30	200	0·4	0·0033	−0·0367 (*c*)
0·0400	30	300	0·4	0·0004	−0·0396 (*c*)
0·0400	30	500	0·4	0·0004	−0·0395 (*c*)
0·0400	30	1000	0·4	0·0005	−0·0395 (*c*)

(*a*) End-point slow in coming.
(*b*) The Cu_2I_2 was completely dissolved in KI before titrating.
(*c*) Visible precipitation of Cu_3I_2 took place on titrating the free iodine.

From the results recorded in A it appears that, though the excess of potassium iodide is about 0·2 grm., the amount used being approximately twice that required by the theory, the reaction resulting in the formation of cuprous iodide and liberation of iodine is not quite complete. On the other hand, the results recorded in B show plainly that at similar dilution the reaction yields excellent indications of the amount of copper handled when the amount of potassium iodide is considerably more than the theoretical amount, varying from four to sixty times the amount required by theory, the absolute excess varying from 0·6 to 12·7 grm.; and this is true even though the amount of potassium iodide is sufficient to dissolve completely the cuprous iodide formed.

So it is plain that the amount of potassium iodide used has within limits an influence upon the result. In a volume of about 50 cc. an excess of 0·2 grm. of potassium iodide is not enough, while an excess of 0·6 grm. appears to be sufficient. Beyond this limit the addition of potassium iodide has no appreciable effect. It is natural to suppose that at high dilutions a larger excess of potassium iodide would be needed to complete the reaction than is required at lower dilutions. Table II. contains the results of experiments made to test the efficiency of potassium iodide in precipitating 0·0010 grm. of copper, taken as sulphate, in a volume of 100 cc.

Table II.—*Effect of Potassium Iodide in Neutral Solutions at a Fixed Volume of* 100 cc.

Copper taken as $CuSO_4$.	KI used.	Acid added.	Volume.	Copper found.	Error.
Grm.	Grms.	Cc.	Cc.	Grm.	Grm.
0·0010	1	—	100	0·0003	−0·0007
0·0010	2	—	100	0·0006	−0·0004
0·0010	3	—	100	0·0009	−0·0001
0·0010	4	—	100	0·0009	−0·0001
0·0010	3	—	100	0·0013	+0·0003

From the results of these experiments it appears that while the action upon a milligrm. of copper, taken as the sulphate in 100 cc. of solution containing no free acid, is not completed by 1 grm. or 2 grms. of potassium iodide, it is practically complete when an excess of 3 to 5 grms. of potassium iodide is present. The fact is again emphasised that up to a certain proportion, increasing with the dilution, the amount of potassium iodide influences the completeness of the reaction in neutral solution. An excess of potassium iodide amounting to 0·6 to 1 grm. in a volume of 50 cc., and to from 3 to 5 grms. in a volume of 100 cc., will precipitate completely 0·0020 grm. of copper. In the practical application of these facts it must be borne in mind that it is the excess of potassium iodide and not the full amount added which is important.

So we may very properly fix upon 2 grms. as the uniform amount of potassium iodide suitable for the precipitation of cuprous iodide in a volume of 50 cc. of a neutral solution containing 0·2 grm. of copper; and upon 5 grms. as the amount of potassium iodide suitable in neutral solutions having a volume of 100 cc.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, March 19th, 1908.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President in the Chair.

(Concluded from p. 167).

62. "*The Constitution of Thiocyanates containing an Electronegative Group.*" By AUGUSTUS EDWARD DIXON and JOHN TAYLOR.

Examination of a number of acylthiocarbimides shows the contained ·NCS group to have the same refraction value as in hydrocarbon thiocarbimides; since this holds also for acetyl "thiocyanate" (Hawthorne, *Trans.*, 1906, lxxxix., 556), it seems probable that the ·NCS group is contained equally in acyl "thiocyanates" and acylthiocarbimides, true acyl thiocyanates being still unknown.

Moreover, the partial decomposition with formation of thiocyanic acid characteristic of "acyl thiocyanates" also takes place in the case of acylthiocarbimides, the latter undergoing this change with caustic alkalis or alkaline bases, but not with arylamines. The chemical differences between acyl thiocyanates and acylthiocarbimides are due, not to diversity of constitution, but to the variable resistance offered by the acyl radicle to its separation from the combined ·NCS group; when this is high, thiocarbimidic function preponderates, and when low, thiocyanic decomposition. Hence external circumstances, in so far as they affect that separation, may predominate in determining the direction of change.

Diphenylamine unites with acetyl, benzoyl, carboxymethyl- or carboxyethyl-thiocarbimide, forming an *a*-acyl-*bb*-diphenylthiocarbamide. a-*Acetyl*-bb-*diphenylthiocarbamide*, m. p. 141° (corr.), gives with alcoholic potash aa-*diphenylthiocarbamide*, m. p. 212°, and by distillation yields acetylthiocarbimide, identical with the compound produced from acetyl chloride and metallic thiocyanates; with acetic anhydride, *aa*-diphenylthiocarbamide regenerates *a*-acetyl-*bb*-diphenylthiocarbamide.

a-*Benzoyl*-bb-*diphenylthiocarbamide*, a-*carboxymethyl*-bb-*diphenylthiocarbamide*, and a-*carboxyethyl*-bb-*diphenylthiocarbamide* melt at 135°, 128°, and 125° respectively; by lead or silver salts these trisubstitution compounds are desulphurised with difficulty, or not at all.

a-*Carboxymethyl*-ab-*diphenylthiocarbamide*, isomeric with the *bb*-diphenyl derivative, is obtained from methyl chlorocarbonate and thiocarbanilide; it melts at 106°, and, like *a*-carboxyethyl-*ab*-diphenylthiocarbamide, is desulphurised readily by alkaline salts of silver or lead.

63. "*The Quantitative Conversion of Aromatic Hydrazines into Diazonium Salts.*" By FREDERICK DANIEL CHATTAWAY.

All primary aromatic hydrazines can be quantitatively converted into the corresponding diazonium salts either by chlorine or by bromine.

If either halogen be allowed to act at a low temperature on the hydrazine dissolved in alcohol, the diazonium salt separates out in a pure state.

Unless, however, the solid salt is required, the operation can be most easily carried out by dissolving the hydrazine in glacial acetic acid, cooling the solution to about −15° by the addition of crushed ice, and either passing in a rapid stream of chlorine or adding the calculated quantity of bromine dissolved in acetic acid and similarly cooled by ice.

The formation of the diazonium salt is without doubt effected by a substitution of two atoms of hydrogen in the hydrazino-group by halogen, followed by the elimination of halogen acid, thus :—

$$C_6H_5\cdot N\cdot H \;\Rightarrow\; C_6H_5\cdot N\cdot Cl \;\Rightarrow\; C_6H_5\cdot N\cdot Cl$$
$$\quad\;\; |\qquad\qquad\;\; |\qquad\qquad\;\; |||$$
$$\quad H\cdot N\cdot H \qquad H\cdot N\cdot Cl \qquad\quad N$$

As in other cases where hydrogen attached to nitrogen is replaced by halogen, an additive product is probably first formed, in this instance by the addition of four halogen atoms, each nitrogen atom becoming quinquivalent, the elimination of halogen acid then gives rise to the diazonium salt, which being stable under the conditions of the experiment can be isolated.

64. "*Quantitative Separation of Thallium from Silver.*" By JAMES FREDERICK SPENCER and MARGARET LE PLA.

A quantitative separation of the salts of silver and thallium is effected by treating the mixture with a stream of chlorine, whereby the thallium is oxidised to the very soluble thallic chloride and the silver is precipitated as silver chloride. After removing the latter, the solution is concentrated, and reduced by means of sulphur dioxide (either liquid or gaseous). The excess of sulphur dioxide is removed by boiling, and the thallium precipitated as thallous iodide, filtered, washed, and dried at 140°. The results are quantitative, and are obtained very quickly.

Thallous chloride was found to be more soluble in potassium carbonate than in water, for whereas water dissolves 3·86 grms. per litre at 25°, a 5N-solution of potassium carbonate dissolves 21·84 grms. per litre at the same temperature.

65. "*Molecular Volumes of the Nitrites of Silver, Mercury, and the Alkali Metals.*" By PRAFULLA CHANDRA RAY.

The author finds that the molecular volumes of the nitrites of lithium, sodium, potassium, silver, and mercury are 63·44, 63·98, 88·88, 69·16, and 83·04 respectively.

66. "*Lithium Nitrite and its Decomposition by Heat.*" By PRAFULLA CHANDRA RAY.

Lithium nitrite is a mono-hydrated salt, and does not crystallise with half a molecule of water as stated by Lang.

In its general properties it resembles the nitrites of the other alkali metals.

67. "*The Existence in Aqueous Solutions of a Univalent Cadmium Ion, a Subvalent Thallium Ion, and a Bivalent Bismuth Ion.*" By HENRY GEORGE DENHAM.

The method of continuous circulation used by Denham and Allmand (*Trans.*, 1908, xciii., 424) to prove the existence of a univalent lead ion in aqueous solution has been applied to investigate the existence of similar ions of other metals.

A hot solution of cadmium sulphate was kept circulating over a column of granulated cadmium, and in thirty-six hours well-marked crystals began to appear, proving that the ionic reaction $Cd^{\cdot\cdot} + Cd \rightleftharpoons 2Cd^{\cdot}$ had taken place with absorption of heat, and had been reversed in the cold part of the apparatus.

Granulated thallium, in contact with a solution of

thallous sulphate, gave a similar crystalline deposit in three days, demonstrating the reaction $Tl^{\cdot} + Tl \rightarrow Tl_2^{\cdot}$, and in the light of this experiment it is considered probable that the darkening of thallous haloid salts on exposure to sunlight is due to the formation of coloured sub-haloid salts, analogous to the case of silver.

Bismuth, heated in contact with a solution of the oxychloride in hydrochloric acid, soon gave unmistakable evidence of the production of the ion $Bi^{\cdot\cdot}$, but it is of interest that no evidence for such an ion was obtained in the case of arsenic or antimony. Nickel and nickel sulphate solution showed no signs of crystals, although in this case a suboxide Ni_2O has been described.

68. "*Note on the Oxidation of Phenylhydrazine by Caro's Acid.*" By John Cannell Cain.

In explaining the mechanism of the oxidation of aromatic hydrazines by free oxygen and other oxidising agents, Chattaway (*Trans.*, 1907, xci., 1323; 1908, xciii., 270) assumes the formation of an unstable hydroxyhydrazine which immediately loses water and nitrogen, thus :—

$$\begin{matrix} R & H \\ \dot{N}—H \\ H & OH \end{matrix} \rightarrow \begin{matrix} R{\cdot}H \\ N_2 \\ H{\cdot}O{\cdot}H \end{matrix} .$$

The presence of such a hydroxyhydrazine was not observed by Chattaway, as the oxidation always proceeded with immediate evolution of nitrogen, but striking confirmation of this hypothesis is afforded when phenylhydrazine (1 mol.) is oxidised by Caro's acid (equivalent to 1 atom of oxygen). When ice-cold, neutral, aqueous solutions (saturated with ether) of these agents are mixed together, a greenish-yellow coloration is immediately produced; this persists for some seconds, when vigorous evolution of nitrogen begins, the greenish-yellow coloration gives place to a yellow turbidity, and benzene appears on the surface of the liquid. On extraction with ether, the only products are benzene and azobenzene, no diazo-compound being formed. The same phenomenon is observed if equimolecular amounts of phenylhydrazine and oxygen (as Caro's acid) are used, or if the solutions are rendered slightly alkaline or acid before mixing. It appears highly probable that the greenish-yellow coloration is due to the presence of a hydroxyhydrazine as postulated by Chattaway, and that this then undergoes disruption into benzene and azobenzene.

No explanation is given by Chattaway of the mechanism by which azo-compounds are formed in the reaction, but it seems probable that two molecules of the hydroxyhydrazine may decompose according to the scheme :—

$$\begin{matrix} R{\cdot}NH{\cdot}\ NH{\cdot}OH \\ R{\cdot}NH{\cdot}\ NH{\cdot}OH \end{matrix} \rightarrow \begin{matrix} R{\cdot}NH \\ | \\ R{\cdot}NH \end{matrix} + \begin{matrix} N \\ \| \\ N \end{matrix} + 2H_2O,$$

giving rise (in the case of phenylhydrazine) to hydrazobenzene which would be immediately oxidised to azobenzene.

Confirmation of this is perhaps furnished by Chattaway's isolation, in one experiment using 100 grms. of phenylhydrazine, of a very small amount of a white, crystalline solid melting at 125°. As this substance was not recrystallised, it appears likely that it was hydrazobenzene, which melts at 131° (Gattermann, "Practical Methods of Organic Chemistry," gives 126°).

69. "*Some Reactions of Keten.*" By Frances Chick and Norman Thomas Mortimer Wilsmore.

No better source for the preparation of keten by the "pyrogenic" method than acetic anhydride has been found. With this substance a yield of about 10 per cent of fairly pure keten is readily obtained. Acetone is more easily split up, but the resulting keten is too impure for most purposes. Glacial acetic acid is not attacked by the hot wire.

All attempts to prepare glycollaldehyde by the action of keten on water were unsuccessful, only acetic acid being formed. The aldehyde reactions previously mentioned (*Trans.*, 1907, xci., 1941) were found to be due to traces of formaldehyde in the crude keten. Carefully fractionated samples of keten, such as those used for analysis, did not give the aldehyde reactions. Similarly, with alcohol only ethyl acetate was formed.

Gaseous keten is slightly soluble at the ordinary temperature in benzene, chloroform, carbon tetrachloride, and ether, and very soluble in acetone and in acetic anhydride. Liquid keten is miscible without chemical reaction with most organic solvents which are liquid at its boiling-point, including alcohol.

By the action of liquid hydrogen chloride on liquid keten at the ordinary temperature, acetyl chloride, boiling at 51—52°, was obtained. There was no sign of the presence of chloroaldehyde or of dichloroethyl acetate, but a small quantity of an oil with a terpene-like smell was obtained from the residue. In the same way with liquid hydrogen sulphide, thioacetic anhydride, boiling at 55—58°, was formed.

Keten does not react with oxamide, benzamide, nitrosoaniline, acetyl chloride, amyl nitrite, or ethyl iodide. Also, liquid keten does not react at the ordinary temperature with liquid cyanogen. It reacts slowly, however, with anhydrous hydrocyanic acid, but does not appear to form acetyl cyanide.

70. "*Para- and Meta-nitrosoacetanilide.*" By John Cannell Cain.

Para- and meta-nitrosoacetanilide have been prepared by oxidising the corresponding monoacetylphenylenediamine with Caro's acid.

p-*Nitrosoacetanilide* exists in two modifications: the unimolecular form is green, and melts at 176° with decomposition, whilst the bimolecular variety is colourless, and melts at 180—181° without decomposition.

This appears to be the first instance of both modifications of a nitroso-compound existing in the solid condition.

m-*Nitrosoacetanilide* also exists in two forms: the unimolecular modification, which was not isolated as it could not be obtained free from the bimolecular variety, remains as a green residue from its ethereal solution. This, on crystallisation from alcohol, furnishes the bimolecular form in pale, yellowish-brown needles melting at 111°.

71. "*Labile Isomerism among Acyl-salicylamides and Acyl-hydroxyamines.*" By Arthur Walsh Titherley.

A reply to Auwer's criticism (*Ber.*, 1907, xl., 3506).

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 6th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Mr. W. P. Byrne, C.B., Mr. Greville Douglas, Miss Forbes, Mrs. Hamilton, Mr. W. A. Johnstone, Dr. H. W. McConnel, Mr. A. K. Nicholson, Mr. J. Oswald, J.P., and Mr. J. E. Stead, J.P., F.R.S., were elected Members. The following are the lecture arrangements after Easter:—Mr. Gerald Stoney, two lectures on "The Development of the Modern Turbine and its Application"; Prof. F. T. Trouton, two lectures on (1) "Why Light is Believed to be a Vibration," (2) "What it is which Vibrates" (Experimental Course); Prof. William Stirling, two lectures on "Animal Heat and Allied Phenomena"; Mr. W. Bateson, three lectures on "Mendelian Heredity"; Dr. Alexander Scott, three lectures on "The Chemistry of Photography" (Experimental Course); Mr. G. F. Scott Elliot, two lectures on "Chile and the Chilians"; Mr. Laurence Binyon, two lectures on "Japanese Prints"; and Dr. H. W. Davies, two lectures on "The Art of Bach and Future Developments" (with musical illustrations). The Friday Evening Meetings will be resumed on May 1st, when Prof. Joseph Larmor will deliver a discourse on "The Scientific Work of Lord Kelvin" (with experiments and typical apparatus illustrative of his discoveries and inventions). Succeeding discourses will probably be given by Dr. J. Y. Buchanan, Dr. H. T. Bulstrode, Prof. Dr. J. C. Kapteyn, of the University of Groningen, Sir Ralph Payne-Gallwey, Bart, Prof. Sir James Dewar, and other gentlemen.

NOTICES OF BOOKS.

Stoichiometry. By Sydney Young, D.Sc., F.R.S. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1908.

In many respects this is the most interesting of the series of text-books of physical chemistry yet published, and it seems likely to be the one which will have the widest circulation, for it deals with the fundamental principles of physical chemistry in an admirably clear way. Overlapping with the other volumes of the series has been skilfully avoided, although the title stoichiometry has been interpreted in a wide sense. The introductory chapters deal with the laws of chemical combination and the properties of gases, and then methods of determining atomic weights are described, and the results obtained are tabulated. The Periodic Law is discussed in considerable detail, Lothar Meyer's table being adopted as preferable to Mendeleeff's. The properties of liquids, the kinetic theory of gases, and the properties of solids are next treated, and the chapter on mixtures is perhaps the most difficult in the book; in it the author's own important researches are touched upon. The introduction to the series, by Sir William Ramsay, is printed in this volume, to which it properly belongs.

A Treatise on Chemistry. By H. E. Roscoe, F.R.S., and C. Schorlemmer, F.R.S. Volume II. "The Metals." New Edition. London: Macmillan and Co., Ltd. 1907.

The fourth edition of Sir Henry Roscoe and Prof. Schorlemmer's well known treatise on inorganic chemistry has been thoroughly revised and much enlarged. The second volume now contains the section on chemical crystallography, which was formerly included in the first volume on the non-metallic elements, and much new matter has been added, dealing with recent advances in our knowledge of the chemistry of the metals and their compounds. Thus a new section on the radio-active elements gives a *résumé* of the most important work which has been done on the subject, dating back to the investigation of the phenomena of high vacua in 1870. The metals of the rare earths are treated much more fully than before, and the outline of the methods of separating these elements includes a valuable table which shows very clearly the process of decomposing the original earths. As in the earlier editions, technical processes, for example, glass-making, are treated in sufficient detail for the student of general chemistry, who can base a specialised knowledge of any technical branch very satisfactorily upon the information he will find in the treatise, the most modern processes only being considered.

Technical Dictionary. Vol. II. By Kurt Deinhardt and Alfred Schlomann. Edited by Chas. Kinzbrunner, A.M.I.E.E. London: Archibald Constable and Co., Ltd. 1908.

This technical dictionary in six languages, English, French, German, Italian, Spanish, and Russian, will be a boon to engineers and scientific men generally who have occasion to refer to foreign periodicals and text-books. It is excellently planned and arranged, and although it contains an immense amount of matter, space has been so well economised that it is not by any means of unwieldly size. On the other hand, there is no niggardliness of explanation, nor are any baffling abbreviations used, which often waste much time and patience, and the dictionary is excellently illustrated by clear little diagrams. An alphabetical index is provided, showing where every word is to be found, and although this means looking up an unknown word twice it is undoubtedly the best plan. The present volume deals with all branches of electrical engineering with the exception of traction, which is deferred to a later volume on railway engineering. Telegraphy and telephony are included and a limited amount of electro-chemistry. The dictionary can be confidently recommended as one of the most valuable of its kind to be procured.

British Minerals and Where to Find Them. By J. Stephen Neil, F.G.S., F.C.I.S. London: Thomas Murby and Co.

Students of geology will find this book handy as a reference list giving the minerals, rare and otherwise, which are to be found in Great Britain. It is divided into two parts. In the first the minerals are classified according to the localities in which they occur, so it is very easy for the mineralogist to ascertain what specimens he may expect to find in any district. The second part gives an alphabetical list of minerals, together with short descriptions of their crystalline form, their colour, lustre, and occurrence; some notes on the chemical composition of some of the commoner minerals would probably be appreciated, but the list as it stands will satisfactorily fulfil its chief aim of helping the student to identify specimens which are unknown to him.

Matriculation Directory, January, 1908. Cambridge: The University Tutorial Press.

The Matriculation Directory, No. XLVIII., issued by the University Correspondence College, gives reprints of the papers set in the examination held in January this year, together with solutions of some of them and criticisms of the questions. In addition the book contains a good deal of sound advice on the choice of subjects and methods of preparation, given by tutors who are well acquainted with the scope of the examination and are thoroughly qualified to assist intending candidates.

Merck's 1907 *Index.* Third Edition. New York: Merck and Co.

This book, which is well known as a useful handbook for druggists and doctors, has been enlarged by the addition of the names, physical constants, physiological effects, doses, and therapeutic uses of the newest chemicals and drugs which have come into use recently. The products which can be obtained from the firm of Merck and Co. are all specially marked, but others are also included for the sake of completeness, and although a price list is not given a kind of key is provided by which the comparative costs of the preparations can be ascertained.

Man and His Future. By William Sedgwick. London: T. Werner Laurie. 1907.

A genuine attempt to put before the reading public the scientific facts which seem to show what may be man's ultimate destination and destiny is always to be treated with respect, and this book is a good example of a class of literature which attracts many readers. It is easily written, and the author is an adept at stating his arguments forcibly and driving them well home; he may, perhaps, be forgiven a tendency to didactic writing, for the sake of the obvious loftiness of his aim and the strength of his convictions. The book is well worth reading by those who are interested in endeavours to solve the riddle of the universe, and who like their science in easily digested forms and small quantities.

The Education of To-morrow. By John Stewart Remington. London: Guilbert Pitman. 1907.

The author of this work describes his book as the disconnected notes of a man who has watched very carefully the results of modern English education, but such a view of it does not give an adequate idea of the value of the suggestions he has to offer. Unpretentious as the volume is, it discusses sensible practical views on the best ways of truly educating the mind of a child, and the criticisms of

modern methods, though sweeping and expressed with warmth, are, on the whole, justified. Many of the ideas are by no means new, and, in fact, have been put forward by the best known educationists of the day, who, rejecting traditional methods, aim before all things at the development of the reasoning power, the resourcefulness and initiative of the pupil; but as yet these ideas appear to have made but little headway. The misuse of examinations is another subject which the author discusses, and many of his readers will agree with his opinions, and will perhaps wish that he had explained rather more fully the remedies for a state of affairs which is undoubtedly unsatisfactory in the eyes of thoughtful men.

Technologie der Fette und Ole. ("Technology of Fats and Oils"). By GUSTAV HEFTER. Vol. II. Berlin: Julius Springer. 1908.

IN this comprehensive work the origin, raw material, preparation, properties, and uses of the animal and vegetable oils, fats, and waxes are discussed very fully. Methods of analysis are not included, but all other branches of the fat industry are treated with the greatest completeness, so that the work will be indisensable for chemists and manufacturers. Much statistical material is given, and modern processes are fully explained. Methods of preparation are considered at some length, especially if they are in any way unusual (*e.g.*, as in the case of cotton or palm oil) or otherwise deserving special attention.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 8, February 24, 1908.

Causes of the Allotropic Transformation of Yellow Phosphorus dissolved in Essence of Terebenthene.—Albert Colson.—Yellow phosphorus dissolved in essence of terebenthene is transformed into red phosphorus at 250—280°. This change does not appear to be due to a simple molecular condensation, but rather to be the result of a succession of chemical actions forming a closed cycle. Hydrogen compounds appear to be formed, and if their formation is stopped or diminished, the transformation is also either stopped altogether or retarded.

Isomeric Modification of Hydrated Hypovanadic Acid.—Gustave Gain.—Hydrated hypovanadic acid, $V_2O_4.2H_2O$, is red, but loses its colour when kept from contact with the moisture of the air, and becomes olive-green. This change is not due to hydratation, as it takes place in the perfectly dry acid, and it seems probable that the two hydrates are isomeric modifications. Moreover, the isomeric transformation persists in the salts which are obtained from the two forms. It is, however, possible to get to the same final state by adding to a solution of the sulphates the theoretical quantity of caustic potash necessary to saturate the sulphuric acid in the liquid. The liquid is then decolorised, potassium hypovanadate being formed, and it is no longer possible to distinguish between the two forms.

Action of Sulphosalicyclic Acid on Borax.—L. Barthe.—Borax and sulphosalicylic acid react together to form white crystals of formula—

$$O\begin{cases} B<^{OH}_{OC_6H_3<^{SO_3H}_{COONa}}, \\ B<^{OC_6H_3<^{COONa}_{SO_3H}}_{OH} \end{cases}$$

which are decomposed by hydrochloric acid into sodium chloride, boric acid, and sulphosalicylic acid. The sodium potassium salt, in which the SO_3H groups of the above salt are replaced by SO_3K, can be prepared by saturating the boiling aqueous solution of the crystals with alcoholic potash.

Action of Nascent Hypoiodous Acid upon Acids of General Formula $R—CH=CH—CH_2—CO_2H$.—J. Bougault.—*p*-Methoxyphenylisocrotonic acid, when dissolved in water containing sodium carbonate, gives with iodine the corresponding iodated lactone,—

$$CH_3O—C_6H_4—\underset{O}{\overset{|}{\underset{|}{CH}}}—\underset{|}{\overset{|}{CHI}}—CH_2—CO.$$

In presence of large excess of sodium carbonate *p*-methoxybenzoylacrylic acid is obtained, $CH_3O—C_6H_4—CO—CH=CH—CO_2H$. Methylenedioxybenzoylacrylic acid can be obtained similarly, starting with methylene dioxyphenylisocrotonic acid. Thus, phenylisocrotonic acid and its derivatives substituted in the benzene nucleus, when treated with iodine in presence of a very large excess of sodium carbonate, have their side chains, $R—CH=CH—CH_2—CO_2H$, transformed into $R—CO—CH=CH—CO_2H$.

No. 9, March 2, 1908.

Lithium in Radio-active Minerals.—Sir William Ramsay and Alex. Cameron.—The authors do not think that lithium is the sole product obtained when salts of copper are treated with radium emanation, but that its presence can be explained only by supposing that such a change takes place. They have observed that the weight of the alkaline residue obtained is greater after than before treatment with the emanation, and that the spectrum of the residue shows the yellow sodium lines, and the potassium spectrum is also visible. Hence they are convinced that the decomposition of copper yields members of its group., *i.e.*, the alkaline series, and lithium is the most probable product. The sodium and potassium might be derived from the glass, and experiments to decide this question are in progress. The proportions of the products may depend upon unknown circumstances. It is possible that lithium is not a constant product of the action of the emanation on copper salts, but that the presence of other metals may determine its formation.

Direct Hydrogenation of Aromatic Quinones.—Paul Sabatier and A. Mailhe.—The aromatic quinones may be directly hydrogenated in contact with finely divided nickel at 200°, a good yield of the corresponding hydroquinones being obtained. When the temperature of hydrogenation is lowered the diphenols, which are derived from hydroquinone and its homologues, may fix six atoms of hydrogen in the nucleus, and thus the diols of the cyclohexane series can be obtained.

Oxidation of Platinum.—C. Marie.—Platinum appears to be much more readily oxidised at the ordinary temperature than has hitherto been believed. Thus potassium persulphate, bichromate, chlorate, and permanganate in sulphuric acid solution, and the ferricyanide and permanganate in alkaline solution, all oxidise plates of the metal. Ferric chloride in acid solution and hydrogen peroxide appear to have no action, but hot concentrated (not fuming) nitric acid oxidises the metal. The oxide obtained (PtO_2 ?) is dissociated by heat. It is soluble in hydrochloric acid, and in dilute sulphuric acid in presence of reducing agents.

Syntheses by Mixed Organo-metallic Compounds of Zinc. Ketone Alcohols.—E. E. Blaise and I. Herman.—The acid chloride of oxypivalic acid is transformed by the action of $ZnIC_2H_5$ into acetoxypseudobutylethyl ketone,—

$$CH_3—CO—O—C(CH_3)_2—COCl+Zn<^{I}_{C_2H_5}=$$
$$=CH_3—CO—O—C(CH_3)_2—CO—C_2H_5+ZnICl.$$

When this acetoxyketone is saponified with aqueous potash

the products are formic acid, formic aldehyde, and liquid products, which can be separated into two parts. The first part consists of a mixture of ketones which can be separated into ethyl isopropyl ketone and an unsaturated ketone; the other part is composed chiefly of a polymer of the unsaturated ketone. This latter contains seven atoms of carbon, and its formation can be explained only by supposing that a molecular transformation or else a secondary reaction takes place.

Preparation and Properties of Crystalline *d*-Talite.—Gabriel Bertrand and P. Bruneau.—By a slight modification of the details of E. Fischer's method of reducing *d*-talonic acid the authors have obtained pure crystalline *d*-talite. It forms a crust of crystalline prisms in supersaturated alcoholic solutions. It is very soluble in water and is deliquescent. It fuses at 86°. Its most characteristic compound is the tribenzoic acetal already described by E. Fischer.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xli., No. 4, 1908.

Ketenes.—H. Staudinger and H. W. Klever.—The simplest ketene, $CH_2 : C : O$, can be prepared by the action of zinc on bromacetic acid bromide:—$CH_2Br.CO.Br + Zn = CH_2 : C : O + ZnBr_2$. Ketene boils at −56° and melts at −151°. It has an unbearable odour, recalling chlorine and acetic anhydride. It is poisonous. Metallic chlorides make it polymerise, yielding (in ethereal solution) resinous masses. Tertiary bases also cause polymerisation. With water it gives acetic acid; it decolorises an ethereal solution of bromine, forming bromacetyl bromide. Since it does not react with sodium or potassium powder it is probably not an oxyacetylene, which might be expected to have acid properties, but a true ketene of formula $CH_2 : C : O$.

Quantitative Determination of Phenol-hydroxyl Groups.—J. Herzog and V. Hancu.—Diphenyl urea chloride with phenols gives crystalline urethanes, which when treated with caustic potash give diphenylamine. The preparation and saponification of the phenol urethanes provide a means of determining the phenol hydroxyl groups, for the weight of diphenylamine shows how many hydroxyl groups were present in the corresponding phenol. Since 1 OH (17) in the phenol gives one molecule of diphenylamine (169) the weight of diphenylamine divided by 169/17, gives the weight of hydroxyl.

MEETINGS FOR THE WEEK.

WEDNESDAY, 15th.—Microscopical, 8. "Dendritic Growths of Copper Oxide in Paper," by J. Strachan. "Nature's Protection of Insect Life" (illustrated by Lantern Slides in Three-colour Photography), by F. Enock.

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Applications will be received by the above mentioned up to April 30th, 1908.

(By order)

J. POLGLASE,
Municipal Secretary, Singapore.

Municipal Office, Singapore,
February 8th, 1908.

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THE CHEMICAL NEWS.

VOL. XCVII., No. 2525.

ON THE ORIGIN OF JET.*
II.

By PERCY E. SPIELMANN, A.R.C.S., A.I.C., B.Sc. (Hons.) Lond.

THE present article is based on the results of an examination of some samples of Whitby jet, made at the Eidgenössische Prüfungranstalt für Brennstoffe at Zürich, under the direction of Prof. E. J. Constam.

The substance was considered from the point of view of of a fuel; chemical analyses and determinations of heating values were made for comparison with similar results for coals of various kinds, examined in the ordinary routine of such a laboratory.

The following analyses and heating values (published here for the first time through the courtesy of Prof. Constam) have been obtained :—

	I. Cals.	II. Cals.	III. Cals.
Heat of combustion of sample, per grm.	8884	8889	8861
Deduct—			
Heat of combustion of sulphur	29	29	28
Water condensed in bomb = 0·6848 grm., of which the heat of evaporation is	411	411	411
Heating power per grm.	8444	8449	8422

Average 8438 cals.

Chemical Composition of Sample.

Moisture (loss of weight, 103° C.)	2·12 per cent
Ash	0·47
Combustible matter	97·46
	100·05

Elementary Analysis (per cent)

	I.	II.	Mean.
C	81·54	81·74	81·64
H	7·33	7·41	7·37
O	6·20	5·99	6·09
N	1·03	1·02	1·03
S	1·31	1·25	1·28
Ash	0·47	0·47	0·47
Moisture	2·12	2·12	2·12
	100·00	100·00	100·00

By means of the formula $81\,C + 290\left(H - \frac{O}{8}\right) + 25S - 6W$ (a modification of Dulong's formula), the calculated heat of combustion works out to 8511 cals., in excellent agreement with the experimental value 8538 cals.

From the above analysis, one obtains :—

Composition of Combustible Matter (per cent).

C	83·81
H	7·57
O	6·25
N	1·06
S	1·31
	100·00

Heating value, 9084 cals.

* The first article appeared in the CHEMICAL NEWS, 1906, vol. xciv., p. 281.

Volatile Matter.

A determination was made by strongly heating a portion of the same sample in a platinum crucible :—

Volatile matter	74·62 per cent
Moisture	2·12
Ash	0·47
Fixed carbon	22·79
	100·00

The coke remaining behind possessed a graphitic lustre, and showed slight intumescence.

Another sample—from which the external shaly layer, which all jet possesses, was not removed—was extracted with CS_2. 1·9991 grm. of jet yielded 0·3424 grm. (= 17·13 per cent) of a yellow oil, which still contained some CS_2. After drying in vacuum over P_2O_5, until the weight had become constant, the residue consisted of 0·1427 (= 7·14 per cent) of a thick dark brown oil, smelling like petroleum.

The solid matter left behind was pulverised and examined.

	Cals.	Cals.	Cals.
Heat of combustion of sample, per grm.	6722	6715	6719
Deduct—			
Heat of combustion of sulphur	17	17	17
Water condensed in bomb = 0·531 grm., of which the heat of evaporation is	319	319	319
Heating power, per grm.	6386	6379	6383

Average 6383 cals.

Chemical Composition (per cent).

Moisture	2·02
Ash	22·01
Combustible matter	75·97
	100·00

Elementary Analysis.

	I.	II.	Mean.
C	63·81	63·56	63·69
H	5·62	5·74	5·68
O+N	5·80	5·93	5·86
S	0·74	0·74	0·74
Ash	22·01	22·01	22·01
Moisture	2·02	2·02	2·02
	100·00	100·00	100·00

Composition of Combustible Matter (per cent).

C	83·84
H	7·48
O+N	7·71
S	0·97
	100·00

This very closely approximates to the formula $C_{14}H_{16}O$; in which C = 84, H = 8, O = 8 per cent.

Heating value = 8823.

It has been shown that jet consists of approximately 93 per cent of solid matter and 7 per cent of oil. Assuming for a moment that the oil is actually petroleum, with an average heating-power of 11,100 cals. per grm., the total heating-power can be calculated :—

8823 × 92 per cent	= 8205 cals.
11,100 × 7 ,,	= 777 ,,
	8982

in good agreement with 9084 cals. found.

Comparing the results for the above sample of pure jet with those obtained for cannel coal, a great similarity between the two is seen.

Cannel Coal from Ruhr, Westphalia.

	I.	II.
Heat of combustion of sample, per grm.	8629	8646
Deduct—		
Heat of combustion of sulphur	17	17
Water condensed in bomb = 0·5719 grm.. of which the heat of evaporation is ..	343	343
Heating power per grm.	8269	8286

Average.. .. .. 8277 cals.

Chemical Composition of the Sample (per cent).

Moisture	0·73
Ash..	5·50
Combustible matter	93·77
	100·00

Elementary Analysis (per cent).

C	81·44
H	6·27
O	4·11
N	1·20
S	0·75
Ash..	0·73
Moisture	5·50
	100·00

Heating value (calculated), 8281 cals.

Composition of Combustible Matter (per cent).

C	86·85
H	6·69
O	4·38
N	1·28
S	0·80
	100·00

Heating value, 9194 cals.

Volatile Matter (per cent).

Volatile matter	43·59
Moisture	0·73
Ash..	5·50
Fixed carbon	50·18
	100·00

(These analyses were also made at the Eidgenössische Prüfungsanstalt für Brenstoffe, Zürich).

That there should be a difference in the amount of fixed carbon is not surprising, since jet and cannel coal have been formed at different geological periods, probably from very different woods, and certainly under different conditions.

Comparing, in tabular form, the analyses and heating values of the combustible matter of jet and cannel coals from Ruhr and Wigan, the connection between the three is apparent.

	Cannel coal from Wigan (*a*).	Cannel coal from Ruhr.	Jet.
C	85·20	86·85	83·81
H	6·07	6·69	7·57
O	8·58	4·38	6·25
N		1·28	1·06
S		0·80	1·31
	99·85	100·00	100·00
Heating powers (cals.)		9194	9084

(*a*) Muspratt, "Handbuch der Technischen Chemie," 4th German edition, 1893, quoting from Percy's "Metallurgy."

Muck ("Chemie der Steinkohle," Second Edition, 1893) states that jet must be classed with cannel coal, but gives no reasons for it.

These results show that jet must be classed with cannel coal rather than with lignite (av. 5500 cals.), whose composition is very different from the above. Although analogous results for bitumen have not been published anywhere to my knowledge, a calculation made on an average sample gave, as result, a heating value of 10,019 cals.

From this, together with analyses (in my first paper), it is seen that jet is far removed from bitumen, compared with cannel coal.

Mr. McIntosh (CHEMICAL NEWS, 1906, xciv., p. 314) contributes some very interesting facts and suggestions in connection with the origin of jet, and although he is able to speak with a certain amount of authority, I would venture to oppose his attempt to connect jet and amber closely together when considering the former's origin. Taking his letter point by point the following suggestions occur to me :—

In forming a mental picture of the structure of jet on the basis of the extraction experiment mentioned above, it is not unjustifiable to consider each particle of jet to be surrounded by a film of the petroleum-like substance ; this may cause all the difference between the electrifying power of jet and cannel coal, since the petroleum film would act as an insulator and prevent the escape of electricity, just in the same way as an insulating handle permits of the electrifying of a metal rod.

Mr. McIntosh must not think me carping if I consider that an authority about 125 years old to be somewhat out of date for the present argument, especially as Bishop Watson—though fairly correct in his description of the amber beds (compare Geikie, "Text-book of Geology," 1903, ii., p. 1257)—considers amber to be a mineral the production of which requires the aid of subterranean distillation and a mineral acid. Indeed, Mr. McIntosh favours throughout the destructive distillation theory for the origin of petroleum and natural bitumens, while no direct evidence of any source of heat—volcanic or otherwise—has been found when these and other connected substances are studied *in situ*. I do not know if he bases his contention on Neuburger and Noalhat's "Technology of Petroleum," as I was unable to consult this work when collecting authority for my first paper.

If there is any close connection between jet and amber (or resin), it can only be in the relation wood → jet → amber, because jet still contains some recognisable woody structure, which would be impossible if it were derived from amber ; more especially as amber was originally a semi-liquid, able to catch up insects as it moved, and could therefore only exhibit either a flow or crystal structure.

Amber first appears in the Oligocene age. If jet is metamorphosed amber or resin, one would expect to find intermediate gradations between the two bodies in beds later than Upper Lias and earlier than Oligocene ; but none are recorded. Considering, also, that pine resins (and I imagine the resins of all conifers) contain turpentine or some analogous substance of a germicidal character, it is scarcely likely that amber would suffer the particular kind of decomposition (very probably fermentation, and bacterial rather than fungoid) that has changed wood into jet (according to my idea). This, combined with the fact that in such trees as provide resins, these latter, which are waste-products, are thrown out down special ducts, and are not spread promiscuously throughout the cells making up the bulk of the tree, can be taken as strong evidence against Mr. MacIntosh's interpretation of the "jetisation" of the partially fossilised tree, as given in his postscript ; and, indeed, against his general suggestion.

I scarcely agree with Mr. McIntosh's suggestion that the study—by destructive distillation—of possible substances would help in the elucidation of the origin of jet. Differences in the materials from which jet, coal, and amber

(for instance) are formed, to say nothing of the influence of the actual conditions under which the trials would be carried out, would prevent comparable results from being obtained. From what is known, however, the results of distilling the above substances are very different.

Finally, it really goes against the grain that Mr. McIntosh should claim my theory as "a plea for the resiniferous origin of petroleum and jet"! Considering the relative quantities of resin and the tree containing it, and the relative sizes and quantities of the lumps of amber and jet found, the former could only be responsible for a very small quantity of the jet found.

I follow Mr. McIntosh in hoping that the question will be attacked by chemists. So far as I could discover, up to the time of my first paper, no chemist had looked into the question of the origin of jet, only botanists or geologists; these latter have, I think, collected quite enough information for the chemists to work on.

ON THE CALCULATION OF THERMO-CHEMICAL CONSTANTS.

II.

By H. STANLEY REDGROVE, B.Sc. (Lond.).

Thermal Constants of Organic Halogen Compounds.

It is evident from a consideration of the molecular heats of combustion and molecular heats of formation of the hydrocarbons (Chemical News, xcv., 301; xcvi., 188) that, in general, the former are more suitable for the calculation of constants than the latter, and constitute better criteria for the examination of any hypotheses on the subject. This is due to the fact that a small percentage error made in determining a molecular heat of combustion will very often occasion a large percentage error in the corresponding molecular heat of formation.

To take an example, consider benzene: the experimental molecular heat of combustion (corrected) is 797·9 cals. (Thomsen); suppose the mean error to be only 0·2 per cent, this would cause an error of 1·6 cals.; supposing the heats of combustion of carbon and hydrogen in the molecular condition to be known accurately, we get, even in this extreme case, a value, − 13·7 cals., for the molecular heat of formation with a mean error of 1·6 cals.; that is to say, 11·6 per cent!

This increase in percentage error will be found in general. We shall therefore, in preference to molecular heats of formation, employ molecular heats of combustion (in all cases corrected for constant volume) upon which to base any arguments; however, for the sake of completeness the molecular heat of formation constants have been obtained, and the molecular heats of formation calculated therefrom.

1. *Molecular Heat of Combustion of Organic Halogen Compounds.*

All halogen substituted hydrocarbons can be theoretically obtained by replacing f hydrogen atoms by f halogen atoms, where f is some integer; we shall therefore require the following constant:—

χ = the algebraic sum of the following heats—(i.) due to the severance of a C.H link; (ii.) due to the combustion of a hydrogen atom (to liquid water), minus the algebraic sum of the following heats; (iii.) due to the severance of a C.Cl(C.Br,C.I) link; (iv.) one-half that due to the formation of a gaseous chlorine (bromine, iodine) molecule; or as it can be more simply written:—

χ = the sum of the following heats—(ii.) due to the combustion of a hydrogen atom (to liquid water); (iii.) due to the formation of a C.Cl(C.Br,C.I) link, minus the sum of the following heats; (i.) due to the formation of a C.H link; (iv.) one-half that due to the formation of a gaseous chlorine (bromine, iodine) molecule.

So that the general halogen substituted hydrocarbon,—

$$nC+2(n+1-a-2b-p-\tfrac{1}{2}f)H+(n+p-a-b-1)L_1+ +aL_2+bL_3+fC.Cl(C.Br, C.I) \text{ links } +fCl(Br,I),$$

can be written—

$$nC+2(n+1-a-2b-p)H+ +(n+p-a-b-1)L_1+aL_3+bL_3-f\chi(\chi_1,\chi_2)= =na-(n+p-a-b-1)\beta-a\gamma-b\delta-f\chi(\chi_1,\chi_2),$$

where χ is used for chlorine, χ_1 for bromine, and χ_2 for iodine.

Before proceeding to calculate the values of these constants, a few regularities in the molecular heats of combustion of the compounds under consideration will be pointed out, using the results of Thomsen, corrected for constant volume.

1. The effect on the molecular heat of combustion, by replacing a hydrogen atom in any hydrocarbon by a chlorine atom, is constant; similarly, the effects produced by replacing the chlorine by bromine, and the bromine by iodine, are respectively constant, as shown in Table I.

2. The effect on the molecular heat of combustion by replacing in turn 1, 2, 3 hydrogen atoms in any hydrocarbon by chlorine is constant. Apparently the replacement of a fourth hydrogen atom produces a less effect, but as the data is scanty, and the difference is in any case small, it has been neglected in the calculations to follow.

This regularity is shown in Table II.

3. The mere position of the halogen has no effect on the molecular heat of combustion. This is shown by the fact that the results for monochlorpropylene (=452·4 cals.) and for allyl chloride (=453·7 cals.) are practically equal, and the result for ethylene chloride (=295·8 cals.) identical with that for ethylidene chloride (=295·8 cals.).

In Table III. will be found the molecular heats of combustion (corrected for constant volume) of fourteen chlorine, four bromine, and two iodine compounds determined by Thomsen, from these the values of χ, χ_1, and χ_2 have been calculated; thus, methyl chloride is CH_3Cl, *i.e.*, $a-\chi$; M.H.C. found = 176·2 cals. Therefore, $\chi = a - 176{\cdot}2$ cals. = (210·8 − 176·2) cals. = +34·6 cals., &c.

The value thus obtained from each substance is given in the table, and means have been struck so as to give the lowest average error.

The values thus obtained are—

χ = 35·5 cals., χ_1 = 28·6 cals., χ_2 = 15·9 cals.

These are the fundamental molecular heat of combustion halogen constants.

Using these values, the molecular heats of combustion of all the halogen compounds given have been calculated, and the results, together with the difference between them and the experimental, and the percentage error are given in Table III.

Excepting chloroform, perchlorethylene, and carbon tetrachloride the results are quite satisfactory, although not exhibing the extraordinary exactness with which the molecular heats of combustion of hydrocarbons can be calculated by means of the author's "fundamental constants."

2. *Molecular Heat of Formation of Organic Halogen Compounds.*

The constants required will be entirely analogous to the molecular heat of combustion constants, so that:—

χ' = the algebraic sum of the following heats:—(i.). One-half that due to the decomposition of a hydrogen molecule; (ii.) due to the formation of a C.H link minus the algebraic sum of the following heats; (iii.) one-half that due to the decomposition of a chlorine molecule; (iv.) due to the formation of a C.Cl link; or as it can be more simply written—

χ' = the sum of the following heats—(ii.) due to the formation of a C.H link; (iii.) one-half that due to the formation of a chlorine molecule minus the sum of the following heats; (i.) one-half that due to the formation of

TABLE I.

	Hydride. Cals	Difference. Cals.	Cl loride. Cals.	Difference. Cals.	Bromide. Cals.	Difference. Cals.	Iodide. Cals.
Methyl	210·8	−34·6	176·2	+7·8	184·0	+11·4	195·4
Ethyl..	369·0	−35·9	333·1	7·7	340·8	11·9	352·7
Propyl	527·5	−36·4	491·1	7·9	498·0	—	—

TABLE II.

		M.H.C. Cals.	Difference. Cals.
Ethane	C_2H_6	369·0	
Ethyl chloride	C_2H_5Cl	333·1	35·9
Ethylene chloride	$C_2H_4Cl_2$	295·8	37·3
Monochlorethylene chloride	$C_2H_3Cl_3$	262·3	33·5
Methane	CH_4	210·8	
Methyl chloride	CH_3Cl	176·2	34·6
Chloroform	$CHCl_3$	107·2	2×34·5
Carbon tetrachloride	CCl_4	76·5	30·7

TABLE III.—Organic Halogen Compounds.

1. Substance.	2. Formula.	Molecular Heat of Combustion. 3. Formula.	4. M.H.C. found (Thomsen) constant vol. Cals.	5. χ Calculated. Cals.	6. M.H.C. calculated. Cals.	7. Difference between cols. 4 and 6. Cals.	8. Error. Per cent.	Molecular Heat of Formation. 9. Formula.	10. M.H.F. found (Thomsen) constant vol. Cals.	11. χ′ Calculated. Cals.	12. M.H.F. calculated. Cals.	13. Difference between cols. 10 and 12. Cals.
Chlorides.												
Methyl chloride	CH_3Cl	$\alpha-\chi$	176·2	34·6	175·3	−0·9	−0·51	$a'-\chi'$	22·0	−0·8	22·9	+0·9
Ethyl chloride	C_2H_5Cl	$2\alpha-\beta-\chi$	333·1	36·0	333·6	+0·5	+0·15	$2a'-\beta'-\chi'$	29·6	−2·2	29·1	−0·5
Propyl chloride	C_3H_7Cl	$3\beta-2\gamma-\chi$	491·1	36·3	491·9	+0·8	+0·16	$3a'-2\beta'-\chi'$	36·0	−2·4	35·3	−0·7
Isobutyl chloride	C_4H_9Cl	$4\alpha-3\delta-\chi$	648·5	37·2	650·2	+1·7	+0·26	$4a'-3\beta'-\chi'$	43·1	−3·3	41·5	−1·6
Monochlorethylene	C_2H_3Cl	$2\alpha-\gamma-\chi$	297·6	35·0	297·1	−0·5	−0·17	$2a'-\gamma'-\chi'$	−2·5	−1·1	−1·9	+0·6
Monochlorpropylene	C_3H_5Cl	$3\alpha-\beta-\gamma-\chi$	452·4	38·5	455·4	+3·0	+0·66	$3a'-\beta'-\gamma'-\chi'$	+7·3	−4·7	+4·3	−3·0
Allyl chloride	C_3H_5Cl	$3\alpha-\beta-\gamma-\chi$	453·7	37·2	455·4	+1·7	+0·37	$3a'-\beta'-\gamma'-\chi'$	5·9	−3·3	4·3	−1·6
Ethylene chloride	$C_2H_4Cl_2$	$2\alpha-\beta-2\chi$	295·8	$73·3\times\frac{1}{2}$	298·1	+2·3	+0·78	$2a'-\beta'-2\chi'$	33·1	$-5·7\times\frac{1}{2}$	30·8	−2·3
Ethylidene chloride	$C_2H_4Cl_2$	$2\alpha-\beta-2\chi$	295·8	$73·3\times\frac{1}{2}$	298·1	+2·3	+0·78	$2a'-\beta'-2\chi'$	33·1	$-5·7\times\frac{1}{2}$	30·8	−2·3
Dichlorpropane	$C_3H_6Cl_2$	$3\alpha-2\beta-2\chi$	453·0	$74·4\times\frac{1}{2}$	456·4	+3·4	+0·75	$3a'-2\beta'-2\chi'$	40·3	$-6·7\times\frac{1}{2}$	37·0	−3·3
Chloroform	$CHCl_3$	$\alpha-3\chi$	107·2	$103·6\times\frac{1}{3}$	104·3	−2·9	−2·71	$a'-3\chi'$	23·5	$-2·3\times\frac{1}{3}$	26·3	+2·8
Monochlorethylene chloride.	$C_2H_3Cl_3$	$2\alpha-\beta-3\chi$	262·3	$106·8\times\frac{1}{3}$	262·6	+0·3	+0·11	$2a'-\beta'-3\chi'$	32·8	$-5·4\times\frac{1}{3}$	32·5	−0·3
Carbon tetrachloride	CCl_4	$a-4\chi$	76·5	$134·3\times\frac{1}{4}$	68·8	−7·7	−10·07	$a'-4\chi'$	20·5	$+0·7\times\frac{1}{2}$	28·0	+7·5
Perchlorethylene	C_2Cl_4	$2\alpha-\gamma-4\chi$	195·7	$136·9\times\frac{1}{4}$	190·6	−5·1	−2·61	$2a'-\gamma'-4\chi'$	−1·7	$-1·9\times\frac{1}{4}$	3·2	+4·9
		Mean	$\chi = 35·5$					Mean	$\chi' = -1·7$			
Bromides.				χ_1						χ_1'		
Methyl bromide	CH_3Br	$a-\chi_1$	184·0	26·8	182·2	−1·8	−0·98	$a'-\chi$	+14·2	+7·0	16·0	+1·8
Ethyl bromide	C_2H_5Br	$2\alpha-\beta-\chi_1$	340·8	28·3	340·5	−0·3	−0·09	$2a'-\beta'-\chi_1'$	21·8	5·6	22·2	+0·4
Propyl bromide	C_3H_7Br	$3\alpha-2\beta-\chi_1$	498·0	29·4	498·8	+0·8	+0·16	$3a'-2\beta'-\chi_1'$	29·1	4·5	28·4	−0·7
Allyl bromide	C_3H_5Br	$3\alpha-\beta-\gamma-\chi_1$	461·1	29·8	462·3	+1·2	+0·26	$3a'-\beta'-\gamma'-\chi_1'$	−1·5	4·1	−2·6	−1·1
		Mean	$\chi_1 = 28·6$					Mean	$\chi_1' = +5·3$			
Iodides.				χ_2						χ_2'		
Methyl iodide	CH_3I	$a-\chi_2$	195·4	15·4	194·9	−0·5	−0·26	$a'-\chi_2'$	+2·8	18·4	+3·3	+0·5
Ethyl iodide	C_2H_5I	$2\alpha-\beta-\chi_2$	352·7	16·4	353·2	+0·5	+0·14	$2a'-\beta'-\chi_2'$	9·9	17·5	9·5	−0·4
		Mean	$\chi_2 = 15·9$					Mean	$\chi_2' = 17·95$			

a hydrogen molecule; (iv.) due to the formation of a C.Cl link.

Similarly, χ_1' for bromine, and χ_2' for iodine.

It follows therefore that $\chi' + \chi = \chi_1' + \chi_1 = \chi_2' + \chi_2$ = the heat due to the combustion of a hydrogen atom (to liquid water), less half the heat due to the formation of a hydrogen molecule = the heat of combustion of 1 grm. molecular hydrogen to liquid water = $\frac{1}{2} \times 67{\cdot}5$ cals. = 33·75 cals.

Whence—

$$\chi' = (33{\cdot}75 - 35{\cdot}5) \text{ cals.} = -1{\cdot}75 \text{ cals.}$$
$$\chi_1' = (33{\cdot}75 - 28{\cdot}6) \text{ cals.} = +5{\cdot}15 \text{ cals.}$$
$$\chi_2' = (33{\cdot}75 - 15{\cdot}9) \text{ cals.} = 17{\cdot}85 \text{ cals.}$$

In Table III. will be found the molecular heats of formation of the halogen compounds under consideration, given by Thomsen; from these the values of χ', χ_1', and χ_2' have been calculated in a similar manner as were the molecular heat of combustion constants.

The values thus obtained are $\chi' = -1{\cdot}7$ cals., $\chi_1' = +5{\cdot}3$ cals., $\chi_2' = 17{\cdot}95$ cals., agreeing with the above.

Using the mean values—

$\chi' = -1{\cdot}7$ cals., $\chi_1' = +5{\cdot}2$ cals., $\chi_2' = 17{\cdot}9$ cals.,

which are the fundamental molecular heat of formation halogen constants, the molecular heats of formation of all the halogen compounds given have been calculated, and the results, together with the difference between them and experimental, are given in Table III.

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NOTE. — The following is probably the explanation why, in trying to find a formula for the carbon molecule (CHEMICAL NEWS, xcvii., 37) which would give a heat of combustion in agreement with the experimental, it was found invariably that the calculated was too great: constants were employed to determine the formula of a solid substance which were derived from the heats of combustion of gases; this ought only to be done if the latent heat of the solid substance (carbon in this case) were solely due to the splitting up of complex molecules into more simple ones, otherwise the calculated result must of necessity be too great, as in the above case,

ERRATA.—I find two insignificant clerical errors in Table I. (CHEMICAL NEWS, xcv., 301). The figures in Column 4 for di-isopropyl and *iso*-amylene should be 996·6 and 805·6 respectively; corresponding slight changes in the other columns for these two substances are thereby necessitated.

THE COMPOSITION OF THE RED CLAY.

By F. W. CLARKE.

IN the volume upon "Deep Sea Deposits" (pp. 198, 201, 425—35), issued as one of the reports of the *Challenger* expedition, there are published twenty-five analyses of the "red clays." This sediment is now recognised as the most extensive and important of all oceanic deposits, for it covers 51,500,000 square miles of the sea floor, and is characteristic of the greatest depths. It is therefore obviously desirable to know its average composition as exactly as possible, and for that reason the following investigation was undertaken.

Of the analyses above mentioned twenty-one were by Brazier, two by Hornung, one by Klement, and one by Renard. They are, however, not strictly comparable, as a glance at the recorded data will show, nor are they, from the point of view of the modern analyst, so complete as they should be. For example, that ubiquitous element, titanium, was not determined in any of the analyses, for at the time they were made its importance and relative abundance were not appreciated. Other substances which are common in clays were neglected for similar reasons, but their significance is now better understood, and improvements in analytical methods have made it easier to search for them. In Brazier's analyses the alkalis were not estimated, but were reported by the other analysts; an omission in the first group that was not due to oversight, but to the limitations of the purposes for which the work was done. The general nature of the red clay was well established, its great variability in composition was clearly shown, and its relations to other clays were made sufficiently plain to satisfy all ordinary requirements.

Of late years, however, it has become a matter of interest to determine the relative abundance and distribution of the chemical elements; and in an inquiry of that sort so notable a substance as the red clay could not well be neglected. A new and more elaborate analysis of it therefore seemed to be required, and to that end two methods of investigation were available. First, it was possible to make a number of individual analyses of separate samples, from which an average might be computed. Secondly, one composite sample could be analysed, giving the desired information once for all. The first method, evidently, would have involved much labour, too much, indeed, to be justifiable. The second method would solve the problem equally well, but with greater ease and vastly less expenditure of time. The second, therefore, was chosen. Through the kindness of Sir John Murray, and his secretary, Mr. James Chumley, fifty-one samples of the red clay, from as many localities, and approximately equal in weight, were combined into a single sample, and that was analysed by my associates in the Laboratory of the United States Geological Survey. (The analytical methods employed were those prescribed by Hillebrand, in *Bulletin* No. 305, U.S. Geological Survey). The results of the composite analysis will be given presently.

The composite sample, as made up by Mr. Chumley, contained thirty-five samples from the dredgings of the *Challenger* expedition, twelve collected by the *Egeria*, two by the *Waterwitch*, and two by the *Penguin*. Of these, eight samples were collected in the Atlantic, two in the Indian Ocean, and forty-one in the Pacific. The *Challenger* localities were stations Nos. 5, 9, 26, 27, 29, 160, 165, 181, 215, 221, 226, 228, 229, 230, 238, 240, 241, 244, 247, 251, 253, 254, 255, 256, 258, 259, 275, 277, 285, 286, 288, 294, 329, 330, and 353. These stations can be identified by reference to the published reports of the expedition. (A chart showing the position at which each sample was taken was also furnished with the material sent for analysis). The geographic range of the collection is evidently large enough to give a significant average, and the number of individual samples was also adequate. Twelve of the localities enumerated above are represented among the analyses already published in the volume on "Deep Sea Deposits," and are there indicated by their station numbers. The other localities furnished material hitherto unstudied chemically.

The new analysis of the clay was made made upon the air-dried and unwashed sample. It therefore included adherent sea salts, and hygroscopic moisture, varying in these respects from the earlier analyses. The magnitude of these variations, however, was determined, and appears in Table I. The final data are as follows:—

A. General analysis, by Mr. George Steiger.
B. Portion solution in cold water, by Mr. George Steiger.
C. Special determinations, by Dr. W. F. Hillebrand.
D. Special determinations, on material concentrated from 150 grms. of clay, by Dr. E. C. Sullivan.

These last determinations were checked by blank experiments upon equal quantities of the reagents employed in the research. Zirconia and the rare earths were sought for by Dr. Hillebrand, but not found. Titanium, chromium, vanadium, barium, strontium, nickel, copper? lead, zinc, arsenic, and molybdenum were not reported in the *Challenger* analyses. Their widespread distribution in the igneous rocks is, however, well recognised. The absence of lithium and fluorine is noteworthy. The unusually high

proportion of manganese suggests the presence of disseminated or incipient manganese nodules, like that so admirably analysed by Gibson ("Deep Sea Deposits," p. 422). In his work several of the rarer elements were determined; so that their existence in the oceanic sediments is no new discovery. The fact of their general distribution, however, remained to be proved.

TABLE I.

	A.	B.	C.	D.
SiO_2	45·32	none		
Al_2O_3	13·26	none		
Fe_2O_3	7·20	none		
FeO	0·70	none		
MgO	3·05	0·21		
CaO	6·82	0·19		
Na_2O	3·63	} 2·01		
K_2O	2·43			
H_2O at 106°	3·28	—		
H_2O above 106	5·93	—		
TiO_2	0·82	—		
CO_2	3·91	—		
P_2O_5	0·25	—		
SO_3	0·48	0·39		
Cl	2·77	2·73		
F	none	—		
Cr_2O_3	0·01	—	0·011	
NiO, CoO	0·032	—		
MnO_2	1·01	—		
BaO	0·17	—	0·16	
SrO	0·046	—		
Li_2O	none	—		
V_2O_3	0·023	—	0·035	
MoO_3	—	—	trace	
CuO	—	—	—	0·02
PbO	—	—	—	0·007
ZnO	—	—	—	0·004
As_2O_3	—	—	—	0·0007
	101·141	5·53		
Less O = Cl	0·62	0·62		
	100·521	4·91		

In order to establish the true composition of the clay substance, some deductions must be made from the analysis as it is now stated. Hygroscopic water and soluble matter must be eliminated, and also the calcium carbonate which is represented by the CO_2. The composition of the aqueous extract, as given by Mr. Steiger's figures, is very near that of the sea salts. I have therefore taken Dittmar's analysis of sea salts as a standard, and subtracted their equivalent, as measured by the chlorine in the unleached clay, from the analysis of the latter. A slight excess of SO_3 remained, which I have also thrown out as representing gypsum. In short, from the general analysis I have withdrawn the water lost below 106°, the sea salts, the calcium carbonate, and a little gypsum, and re-calculated the remainder to 100 per cent.

For comparison, I have combined the twenty-five analyses of the *Challenger* report into an average, from which similar subtractions, so far as they were needed, have been made. In this case only gypsum and calcium carbonate were rejectable. As for the combination, its value is not very great, because of the inequality shown by the individual analyses. Only in four of the latter were alkalis determined, and the mean of those four I have assumed to be representative of all. The ferrous oxide is even more doubtful, for it was only determined in one of Hornung's analyses and neglected in the others. Still, as will be seen in Table II., the comparison is not without significance, and even if it is not perfect, it is better than none at all.

The minor elements, not shown in the *Challenger* analyses, only sum up, altogether, to 1·36 per cent. Apart from these the comparison is satisfactory in some respects, not so in others. In silica, alumina, and water, the agreement is fairly good, but in iron the old analyses range much higher than the new. Possibly for the individual analyses, the reddest and therefore the most ferruginous samples were chosen for examination, as being presumably the most typical.

TABLE II.—*Reduced Analyses.*

	Composite analysis.	Challenger average.
SiO_2	54·48	54·28
TiO_2	0·98	—
Al_2O_3	15·94	16·41
Cr_2O_3	0·012	—
Fe_2O_3	8·66	13·58
FeO	0·84	1·26
NiO, CoO	0·039	—
MnO_2	1·21	1·62
MgO	3·31	1·76
CaO	1·96	0·74
SrO	0·056	—
BaO	0·20	—
K_2O	2·85	1·61
Na_2O	2·05	1·37
V_2O_3	0·035	—
As_2O_3	0·001	—
MoO_3	trace	—
P_2O_5	0·30	0·35
CuO	0·024	—
PbO	0·008	—
ZnO	0·005	—
H_2O	7·04	7·02
	100·000	100·00

On the proximate or mineralogical composition of the red clay I have no important suggestions to offer. That problem was discussed at some length, in the *Challenger* report, on the basis of Brazier's analyses. In those analyses there was discrimination between the portion of the clay soluble in strong hydrochloric acid and the portion insoluble. In nearly every case the soluble ferric oxide was reported in excess of the insoluble; from which I am inclined to suspect that the iron of the clay is present, at least partially, in limonitic or glauconitic combination. The new composite analysis shows a quantity of potash, which suggests the presence of glauconite. The latter compound may well exist in a diffused form, quite unlike its common granular variety, and therefore not so readily recognised. This is a mere suspicion, not entitled to much weight at present, but worth considering in future investigations. My specific problem has been to study the distribution of the chemical elements in nature, and to that end the composite analysis of the red clay is a step forward.

Addendum.

Since the foregoing was written I have received from Sir John Murray a composite of fifty-two "Terrigenous" clays, dredged up from oceanic depths ranging from 140 to 2120 fathoms. In the nomenclature of the *Challenger* expedition, forty-eight of the individual samples are classified as "blue muds" and four as "green muds." Twenty-three of the clays were collected by the *Challenger*; the others were brought in from voyages of the *Buccaneer*, *Dart*, *Egeria*, and *Rambler*. The range of collection, as in the case of the "red clay," was world-wide, and all of the great oceans are represented in the composite sample.

Molybdenum and zirconium were not detected. Nickel, cobalt, lead, zinc, and arsenic, which were reported in the red clay, were not looked for. Apart from these trivial omissions, the red and Terrigenous clays are fairly comparable. The red clay is lower in silica and alumina, but higher in iron than the muds, and other minor differences appear. The high manganese of the red clay may be correlated with the abundance of manganese nodules in the greater oceanic depths. The results of analysis appear in Table III.

TABLE III.

A. General analysis by Mr. Steiger.
B. Portion soluble in water.
C. Analysis reduced to standard form by rejecting soluble salts, calcium carbonate, and hygroscopic water, and re-calculation of the remainder to 100 per cent.

	A.	B.	C.
SiO_2	46·64		57·09
TiO_2	1·04		1·27
Al_2O_3	14·08		17·24
Cr_2O_3	0·044	0·14	0·05
Fe_2O_3	4·14		5·07
FeO	1·88		2·30
MnO	0·10	—	0·12
MgO	1·95	0·18	2·17
CaO	7·20	0·38	2·04
SrO	0·25	—	0·03
BaO	0·05	—	0·06
K_2O	1·84	—	2·25
Na_2O	2·98	2·12	1·05
V_2O_3	0·028	—	0·03
P_2O_5	0·17	—	0·21
CO_2	4·05	—	—
SO_3	0·32	0·32	—
S	0·11	—	0·13
Cl	2·25	2·25	—
CuO	0·016	—	0·02
C	1·38	—	1·69
H_2O at 105°	4·73	—	—
H_2O above 105°	5·86	—	7·18
	100·883		100·00
Less O = Cl	0·56		
	100·323		

—*Bulletin U.S. Geological Survey.*

THE IODOMETRIC DETERMINATION OF COPPER.*

By F. A. GOOCH and F. H. HEATH.

(Concluded from p. 176).

WE have now to study the effect of free acid upon potassium iodide (Table III.).

So it appears that a trifling amount of iodine is in every case set free, due no doubt to presence of traces of iodate. It appears also that no more than 2 cc. of concentrated sulphuric acid or hydrochloric acid may safely be present with 2 grms. of potassium iodide in 50 cc. of solution, and the presence of 1 cc. of pure nitric acid makes error. The tendency to liberate iodine is manifestly less at the higher dilution, and it appears that in a volume of 100 cc. of solution containing 5 grms. of potassium iodide 3 cc. of concentrated sulphuric acid, hydrochloric acid, or nitric acid free from nitrogen oxides may safely be present. Acetic acid of 50 per cent strength may apparently make up half the solution at either dilution. When either sulphuric acid, hydrochloric acid, or nitric acid is present, obviously the higher dilution is preferable.

Table IV. gives the results of experiments in which various amounts of copper were determined by titration of the iodine set free in a volume of 100 cc. in presence of 5 grms. of potassium iodide and free acid.

It appears that so much as 50 cc. of 50 per cent acetic acid may be present with 5 grms. of potassium iodide in 100 cc. of solution without interfering appreciably with the estimation of 0·0010 grm. of copper, and that the error introduced by the presence of 1 cc., 2 cc., and 3 cc. of sulphuric acid, hydrochloric acid, and nitric acid (free from nitrogen oxides) in 100 cc. of solution is scarcely appreciable.

* From the *American Journal of Science*, [4], xxiv., p. 65.

TABLE III.—*Effect of Acids upon Potassium Iodide.*

KI. Grms.	Acid. Cc.	Volume. Cc.	Copper equivalent to I set free. Grms.
	H_2SO_4 (conc.).		
2	1	50	0·0002
2	2	50	0·0005
2	3	50	0·0007
2	5	50	0·0019
5	1	100	0·0002
5	2	100	0·0002
5	3	100	0·0002
5	5	100	0·0014
	HCl (conc.).		
2	1	50	0·0002
2	2	50	0·0003
2	3	50	0·0006
2	5	50	0·0016
5	1	100	0·0002
5	2	100	0·0002
5	3	100	0·0002
5	5	100	0·0008
	HNO_3 (conc., purified).		
2	1	50	0·0025
2	2	50	0·0094
2	3	50	0·0230
5	1	100	0·0002
5	2	100	0·0002
5	3	100	0·0002
5	5	100	0·0294
	$HC_2H_3O_2$ (50 per cent).		
2	25	50	0·0002
5	25	100	0·0002
5	50	100	0·0003

TABLE IV.—*Effects of Acids upon the Determination of Small Amounts of Copper.*

Copper taken as $Cu(NO_3)_2$. Grm.	KI. Grms.	Acid. Cc.	Total volume. Cc.	Copper found. Grm.	Error. Grm.
		H_2SO_4 (conc.).			
0·0010	5	1	100	0·0016	+0·0006
0·0010	5	2	100	0·0014	+0·0004
0·0010	5	3	100	0·0019	+0·0009
		HCl (conc.).			
0·0010	5	1	100	0·0014	+0·0004
0·0010	5	2	100	0·0014	+0·0004
0·0010	5	3	100	0·0015	+0·0005
		HNO_3 (conc., purified).			
0·0010	5	1	100	0·0014	+0·0004
0·0010	5	2	100	0·0015	+0·0005
0·0010	5	3	100	0·0015	+0·0005
		$HC_2H_3O_2$ (50 per cent).			
0·0010	5	10	100	0·0012	+0·0002
0·0010	5	20	100	0·0012	+0·0002
0·0010	5	30	100	0·0010	—
0·0010	5	40	100	0·0010	—
0·0010	5	50	100	0·0010	—

In Table V. are given the results of similar procedure applied to larger amounts of copper.

In the experiments of Series B and C the material for each test was metallic copper standardised electrolytically. Portions of this material were weighed and converted to the nitrate by acting with nitric acid. The solution of the nitrate was evaporated nearly to dryness and the residue dissolved and titrated in the manner indicated.

The N/10 sodium thiosulphate used in estimating the iodine liberated added appreciably to the initial volume, 100 cc., of the solution. In Series A the increase of volume, less than 20 cc., did not affect appreciably the accuracy of the determinations. In Series B the increase of volume to 140 cc., without corresponding increase in

Table V.—*Effect of Acids upon the Determination of Larger Amounts of Copper.*

Copper taken as $Cu(NO_3)_2$.	KI present.	KI, approximate excess.	Acid.	Volume at beginning of titration.	Volume at end of titration.	Copper found.	Error.
Grm.	Grms.	Grms.	Cc.	Cc.	Cc.	Grm.	Grm.
A.—Final volume between 110 and 120 cc.							
			H_2SO_4 (conc.).				
0·1200	5·0	4·5	2·5	100	119	0·1200	—
0·0900	5·0	4·5	3·0	100	114	0·0903	+0·0003
0·0900	5·0	4·5	3·5	100	114	0·0905	+0·0005
			HCl (conc.).				
0·0900	5·0	4·5	2·0	100	117	0·0897	−0·0003
0·1200	5·0	4·5	2·0	100	119	0·1195	−0·0005
0·0900	5·0	4·5	3·0	100	114	0·0901	+0·0001
0·1200	5·0	4·5	3·0	100	119	0·1200	—
0·1200	5·0	4·5	3·5	100	119	0·1197	−0·0003
0·0900	5·0	4·5	4·0	100	114	0·0903	+0·0003
			HNO_3 (conc.).				
0·0900	5·0	4·5	1·0	100	114	0·0900	—
0·1050	5·0	4·5	1·5	100	117	0·1051	+0·0001
0·0900	5·0	4·5	2·5	100	114	0·0901	+0·0001
			$HC_2H_3O_2$ (50 per cent).				
0·1200	5·0	4·5	3·0	100	119	0·1195	−0·0005
0·0900	5·0	4·5	5·0	100	114	0·0898	−0·0002
0·1050	5·0	4·5	10·0	100	117	0·1048	−0·0002
B.—Final volume between 140 and 155 cc. without increase of KI.							
			H_2SO_4.				
0·3336	5·0	3·5	3	100	153	0·3315	−0·0021
			HCl.				
0·2818	5·0	4·0	2	100	144	0·2797	−0·0021
			HNO_3.				
0·3320	5·0	3·5	3	100	152	0·3290	−0·0030
			$HC_2H_3O_2$.				
0·2541	5·0	3·5	6	100	140	0·2523	−0·0018
C.—Final volume increased to 132 and 150 cc., with corresponding increase of KI.							
			H_2SO_4 (conc.).				
0·2218	7·0	6·0	2	100	135	0·2214	−0·0004
0·3231	8·0	6·4	3	100	150	0·3226	−0·0005
			HCl (conc.).				
0·2023	7·0	6·0	2	100	132	0·2016	−0·0007
0·2581	7·8	6·7	3	100	141	0·2574	−0·0007
			HNO_3 (conc., purified).				
0·2023	8·0	7·0	1	100	132	0·2017	−0·0006
0·2520	10·0	8·5	3	100	148	0·2512	−0·0008
			$HC_2H_3O_2$ (50 per cent).				
0·2125	7·5	—	5	100	133	0·2119	−0·0006
0·2064	8·0	—	8	100	132	0·2058	−0·0009

the amount of potassium iodide present, did affect the indications unfavourably.

In Series C, however, the unfavourable effect of similar dilution was overcome by the addition of more potassium iodide.

It is apparent that at any volume a very considerable excess of potassium iodide above the theoretical equivalent involved in the reaction is necessary, and that the necessary excess increases very materially with the dilution of the solution. It appears also that the noted small amounts of sulphuric acid, hydrochloric acid, and nitric acid (free from nitrogen oxides) exert no appreciable influence upon the indications of the process carried out at a volume approximately 100 cc.; and that acetic acid may be present in amount equivalent to at least 25 per cent of the absolute acid.

We find no ground for the inference of Moser that the presence of acid (*Zeit. Anal. Chem.*, 1904, xliii., 597), best sulphuric acid, is necessary to the attainment of good results at all volumes excepting the most concentrated; and there appears to be no reason why the addition of small amounts of acid should increase the amount of iodine liberated if the potassium iodide is free from iodate or other oxidiser. We are wholly unable to offer any explanation for Moser's extraordinary observation, quite contrary to our own, that variation in the amounts of 10N/1 H_2SO_4, from 1 cc. to 100 cc. (0·49 grm. to 49 grms.) for 50 cc. of a solution of copper sulphate, is practically without effect in the treatment by potassium iodide.

The best general procedure in determining by the iodometric method amounts of copper not exceeding about 0·3 grm. seems to us to be covered by the following directions:—The solution of the cupric salt, containing no more than 3 cc. of concentrated sulphuric acid, hydrochloric acid, or nitric acid (free from nitrogen oxides), or 25 cc. of 50 per cent acetic acid, is to be made up to a volume of 100 cc., 5 grms. of iodate-free potassium iodide are to be added, and the titration of the free iodine is to be made by sodium thiosulphate in the usual manner with the use of the starch indicator at the end. In case the end reaction has not appeared when 25 cc. of the thiosulphate have been added, 2 to 3 grms. more of potassium iodide are to be added before continuing the titration.

The error of the process, properly conducted, should not exceed a few tenths of a milligrm. in terms of copper.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, March 27th, 1908.

Dr. Charles Chree, F.R.S., President, in the Chair.

Dr. C. V. Drysdale exhibited a Vacuum Tube Apparatus for demonstrating the Propagation of Alternate Current Waves in Cables.

The propagation of alternate current waves in conductors has been frequently exhibited by the aid of a helix, notably by Prof. Fleming and Dr. G. Scibt, and the former has proposed the use of vacuum tubes to show the distribution of potential. The author had noticed that in a tube laid parallel to the helix the brightness was proportioned to the slope of potential and hence to the current. The apparatus therefore consisted of a wooden stand which supported a helix about six feet long, a vacuum tube just above it, and a series of eighteen vertical tubes below it. On feeding the helix frum a high-frequency resonance circuit nodes and loops of potential and current were simultaneously visible in the two sets of tubes, and these were approximately in quadrature with one another. Experiments were shown in which the frequency of the supply was varied, and the capacity of the helix was altered by introducing an earthed wire inside it. Resistance, capacity, and inductance were also connected successively to the receiving end, and the effects were approximately in agreement with theory.

Mr. W. Duddell expressed his interest in the experiments, and asked why the points of zero potential were not more clearly marked. Was it due to absorption of energy by the tubes or to the superposition of oscillations with higher frequencies? Had the author used a single long tube with a strip of tinfoil on the outside? He also asked what gas the author used in the vertical tubes, and whether he had tried helium.

Dr. Drysdale in reply said that the tubes were filled with CO_2. It was somewhat difficult to ensure their equality, and no attempt had therefore been made to use rare gases. Doubtless still better results could be obtained, but the CO_2 tubes were sufficiently bright for most purposes. He believed that the energy taken by so many tubes was the cause of the absence of complete darkness at the nodes, as with a single tube sharper results had been obtained. For this reason the single tube with a strip of tinfoil on the side had not been used.

Dr. C. V. Drysdale read a paper entitled "*Notes on the Plug Permeameter.*"

The author briefly described the instrument, in which a drill is employed to cut a conical hole in a casting or forging, at the same time leaving a pin one-tenth inch diameter standing in the middle. A wrought-iron plug carrying a bobbin with magnetising and search coils completes the magnetic circuit, forming a miniature permeameter. The readings are taken by means of an ammeter and ballistic galvanometer in the ordinary way, or by the aid of a portable direct-reading test set. When this instrument was first described it was found, as would be expected, that the values of the induction given by it were too low, and it had been supposed by some that this was due to imperfection in the magnetic joint. The author, on the other hand, had attributed it to end effects and to the shortness of the specimen. Investigations had been made confirming this view, and showing that the amount of this end effect could be fairly closely compensated by correcting the value of H in the same ratio for all specimens. These investigations had been carried out by obtaining some rings of cast- and wrought-iron and steel, testing them by the ring method, and afterwards cutting them into quadrants which were drilled and tested with the plug. Curves were given showing the results obtained by the plug permeameter when the instrument had been empirically calibrated from the foregoing tests. These showed that the instrument was accurate within two or three per cent, which was as satisfactory as most other permeameters.

Prof. S. P. Thompson said the author's instrument commended itself for its usefulness and ingenuity. He would like to know how far its results were comparable with those obtained from ring and double yoke methods. He was not sure that the author's explanation that the discrepancies were due to end effects was the correct one. In drilling the hole in the casting the magnetic properties of the iron were altered and the hysteresis increased.

Mr. A. Campbell remarked that from his experience of several varieties of permeameters he was not at all surprised to find that Dr. Drysdale had had to calibrate his permeameter by the purely experimental method of comparison with the trustworthy ring method. By averaging the different calibrations given by various types of material he appeared to be able to obtain fairly good results, but there were other permeameters which gave as satisfactory results without any empirical calibration.

Mr. A. Russell said he appreciated the ingenuity displayed in the Drysdale permeameter. He suggested the following as the probable cause of part of the discrepancy between the magnetisation curves got by the ring method and by the permeameter. In the former method the mean flux and the mean magnetising force over the cross section of the ring were measured. The ring experimented on was of appreciable radial depth, so that the magnetic force on the inner circumference of the ring was about 50 per cent greater than that on the outer circumference. The permeability of the iron at the greater force would probably be very different from that at the smaller force. The mean value, therefore, of the flux density over the cross sectional area of the ring might possibly be something quite different from the value it would have if the magnetic force were constant and equal to the mean magnetic force. The errors due to this cause in the ring method, even when the ring was narrow, were sometimes very appreciable. The criticism also applied to many cases in which electricians apply what they call the fundamental magnetic equation.

Mr. W. Duddell asked if it was assumed that all the pins had the same diameter.

Dr. C. V. Drysdale, in reply to Prof. Thompson, said that the end effect was not of the same nature as an air-gap or it would have had a more marked influence at high permeabilities. When the instrument was first introduced, a few tests had been made by drilling a specimen and testing it, and afterwards annealing and re-testing. No change had been observed, but possibly a greater number of tests would have shown variations. The size of the pin seemed not to vary by more than a mil whatever metal was drilled. As to Mr. Campbell's remarks, he quite agreed that other permeameters were equally or more accurate, but this was the only one that could be used on the actual forging or casting, and it was surprising and gratifying to find that it was as accurate as it seemed to be. The thickness of the ring mentioned by Mr. Russell was an important point. It was necessary in order to permit of drilling, but he was inclined to think that there would be little error from this cause except at low inductions.

Dr. C. V. Drysdale read a paper on "*The Use of Shunts and Transformers with Alternate Current Measuring Instruments.*"

Owing to the limited range of most alternate current instruments shunts and transformers have come into considerable use, but they are liable to cause errors both in the magnitude and phase of the current. The paper deals with these errors mathematically and experimentally. In the case of shunts, the condition for accuracy at all frequencies is that the time constants of the instrument and shunt should be equal, but formulæ are given for the multiplying power and phase displacement in other cases.

For current transformers the best results are obtained by keeping the magnetising and core-loss currents as small as possible. The best uniformity of ratio for different loads is obtained with a non-inductive or leading load; but the lowest phase displacement with a lagging load. P.D. transformers are much more satisfactory than current transformers, both for ratio and phase displacement. Experimental tests using a wattmeter as indicator approximately confirmed the theory.

Mr. A. Campbell expressed his interest in the thorough manner in which Dr. Drysdale had gone into the question of the use of transformers with measuring instruments. With regard to the author's criticism of his (Mr. Campbell's) work on the subject (which was carried out twelve years ago) he should like to mention several points. The main object of the first quoted paper was to show that with air-core transformers the transformation ratio becomes more and more constant (for various frequencies) the higher we make the time-constant of the secondary circuit; thus high inductance and low resistance are wanted. Mr. Campbell stated that in his paper he also gave several experiments to show that iron-ring transformers "may in many cases be used in a similar way," care being taken to have the resistance of the secondary circuit small enough. In a later paper he stated that to make the ratio sufficiently constant and independent of frequency we require relatively low resistance and high inductance in the secondary circuit. Dr. Drysdale showed that, for the special case of constant frequency, relatively high inductance does not give the most constant ratio. His (Mr. Campbell's) experiments were not complete enough to settle this point, and he was careful not to dogmatise on the matter. He was glad that Dr. Drysdale had elucidated it.

Mr. A. Russell expressed his interest in the paper. He suggested that the author should take the mutual inductance between the shunt and the instrument into account. If L_1, R_1 be the constants of the instrument and L_2, R_2, those of the shunt, and if M be the mutual inductance between them, the multiplying factor for the reading will be the same whatever the frequency provided that $\frac{L_1 - M}{R_1} = \frac{L_2 - M}{R_2}$.

Mr. Kenelm Edgcumbe referred to the fact that the author recommended small core-losses, and pointed out that he had seen it stated that in special cases it was possible to improve the ratio and phase errors by increasing the core-losses.

Dr. Drysdale, in reply to Mr. Campbell, said his praise of the air-core transformer was justified, but in practice instrument-makers were forced to use iron for commercial reasons. Similarly, the ring form of transformer was generally impossible, as in practice instrument transformers were used to insulate the observing instrument from high pressure mains, and considerable insulation between the windings was necessary. The reason why an iron-cored transformer behaved differently to one with an air-core chiefly resided in the core-loss current which was not proportional to the magnetising current. The method of testing the transformers would be shown in operation in the laboratories.

A paper on "*Dynamometer Wattmeters*" was read by Dr. C. V. Drysdale.

The author gives a somewhat complete investigation of the theory of the Wattmeter, including the effects of shunt inductance and capacity, mutual inductance, eddy currents, wave-form, and of iron. It is pointed out that the theory of the wattmeter is much obscured by the use of the correction factor. On sine wave forms the true power $\omega = W \cos \phi$, while the reading of the wattmeter—

$$\omega' = \frac{R}{I} W \cos(\phi - a) = W \cos a \cos(\phi \quad a);$$

where W is the apparent power, R and I the resistance and inductance of the shunt respectively, and a the angle of lag in the shunt. This leads to the simple relation—

$$\omega = \frac{\omega'}{1 + T^2 p^2} - T p W \sin \phi;$$

where T is the time constant of the shunt and $p = 2\pi \times$ frequency. In practice $T^2 p^2$ can be neglected in comparison with unity, and hence $d\omega = \omega' - \omega = T p W \sin \phi$, which is perfectly determinate at all power factors. This shows that the correction of a wattmeter should always be applied as a difference and not as a ratio. It is practically as absurd to apply a correction factor to a wattmeter as to an instrument with a zero displacement. The paper also contains a description of some single and double forms of standard wattmeter and of deflectional wattmeters containing iron. Also of the method of testing wattmeters for various errors and of a phase-shifting transformer for facilitating these tests. Various forms of wattmeters and phase-shifters were shown in operation.

Mr. W. Duddell expressed his interest in the paper, referring especially to the author's remarks upon the application of a correction factor. In some ways he thought a correction factor was preferable to the addition of a zero correction. He was interested in the wattmeters exhibited, which resembled in many features an instrument he had designed some years ago.

Mr. Rayner, referring to the accuracy of the instruments, asked if Hooke's law held to one part in 500 over a whole turn of the torsion head.

Mr. Tinsley remarked that the instrument shown resembled those of Mr. Duddell in the mechanical details because the design adopted was the only practical one.

Dr. Drysdale, in reply, said he still maintained that the only rational way of correcting wattmeter readings was by adding a correcting term instead of applying a correction factor. Mr. Beattie's device was unnecessary and of little use, as the inductive coil would not give any indication of the error due to capacity in the shunt, which might be considerable. He had not troubled about astaticism in his instruments as they were for use as standards, and it was easy to eliminate the effect of stray fields. He was surprised and gratified to find that Mr. Duddell recognised the strong resemblance between the wattmeter described in the paper and his own. The author's first paper on the subject appeared in the *Electrician* in March, 1901, and was available to anyone interested in the matter.

SOCIETY OF CHEMICAL INDUSTRY.

(London Section).

Ordinary Meeting, April 6th, 1908.

Dr. J. Lewkowitsch in the Chair.

"*Considerations affecting the 'Strength' of Wheat Flours.*" By Julian L. Baker and H. F. E. Hulton.

It is improbable that any one chemical or physical determination can be correlated with the "strength" of flours, as the generally accepted definition of "strength" includes two distinct qualities, viz., size and shape of loaf. If the bakers would apportion marks independently for size and shape—and there appears to be no reason why this cannot be done—then it would be possible to correlate data obtained in the laboratory with these two factors. We believe that it is in this direction that advances will be made.

The authors were unable to show the presence in flour of a proteolytic enzyme capable of degrading the gluten, and so influencing the character of the loaf, but there are small quantities of an erepsin; that is, a protease capable of degrading the products of pepsin hydrolysis, such as "Witte peptone," and which is characterised by the formation of tryptophane.

The *rôle* played by yeast enzymes in bread making is

discussed, and it is shown that yeast can effect partial proteolysis of gluten. It is probable that the physical character of the gluten may in this way be modified during the early stages of doughing without the production of large quantities of decomposition products.

The importance of amylolytic enzymes in flours is referred to, and evidence is adduced to prove that maltose is the sugar formed during the doughing period. The products of hydrolysis closely resemble those of the action of barley diastase on starch. The character of diastase in flour has been studied, and it is shown that as regards aqueous flour extracts there is a considerable departure from Kjeldahl's law of proportionality. In determining the diastatic power of wheats and flours the reducing power of the solution in terms of maltose should not exceed 20 per cent. No direct relation can be traced between the diastatic power of a flour as measured by Lintner's method and the baker's marks. It is well known that in some cases flours improve on keeping; in this connection it is interesting to note that the diastatic powers of flours also change. Doughs have a greater diastatic activity than either the aqueous extract of the flour or the flour itself, and this diastatic activity varies inversely with the amount of water with which the flour is wetted. This activity increases on keeping the dough at a temperature of 40° C.

The signification of gas production and its relation to "strength" is considered, and it is shown that the gas production follows fairly closely the maltose formed during doughing, which may occasionally rise to 8 per cent. This in conjunction with the circumstance that flour diastase will gradually liquefy flour pastes, suggested the presence of a liquefying enzyme. The malt extract, which is so often used by bakers, is considered to have its main significance as furnishing this liquefying diastase, adequate saccharifying enzyme being already present in the flour. A trace of powdered malt added to flours increases the volume of gas liberated from the dough, and this increase in volume is greater the less the original volume of gas liberated when malt is absent. The percentage increase of gas from malt-activated flours varies from 88 in the case of a flour giving very little gas to nil. This last flour produced a very large original volume of carbon dioxide.

The toxic action of flour and its aqueous extract on yeasts, in view of Lange's work, suggested that different flours might vary in their behaviour to yeast as regards their relative toxicity. Experiment did not confirm this.

The gliadin-glutenin ratio is discussed, and the formation of gluten from these two substances is shown to be independent of enzymic activity, as has sometimes been suggested. It appears to be a hydration phenomenon. Gliadin separated from flour by alcohol was re-combined with the residual gluten and starch, and from this the gluten was recovered by washing out, but in a weakened condition, due partly, doubtless, to the weakening effect of alcohol. The diastatic activity of gluten is confirmed and considered, and this activity is shown to reside in the glutenin moiety.

"*Note on Murexide as a Quondam Dye-stuff and Printing Colour.*" By Watson Smith.

The author exhibited a specimen of commercial murexide manufactured about the year 1861 or 1862, before magenta was able to crush it, as it subsequently did, and also a specimen of calico printed with it which had been carefully preserved from the light, and thus still exhibited the bright rose tints characteristic of it after nearly fifty years. This murexide was manufactured by Robert Rumney, of Manchester, from Peruvian guano, and at one time at the rate of 12 cwts. per week.

It was also pointed out that, although Himmer and Stieglitz indicate the constitution of murexide, and of its basis, purpuric acid, yet thirty years earlier Schorlemmer had pointed to the self-same constitution in his "Chemistry of the Carbon Compounds," published in 1875.

"*The Occurrence of Cyanogenetic Glucosides in Feeding Stuffs.*" By T. A. Henry, D.Sc., and S. J. M. Auld, Ph.D.

It has long been known that a considerable number of plants are capable of yielding prussic acid when ground up and placed in contact with water. In association with Prof. Dunstan the authors have fully investigated a number of these plants, and have shown that the prussic acid is formed by the interaction of a glucoside and an enzyme which decomposes it, liberating prussic acid. Several of these plants are employed as sources of feeding-stuffs, notably Java beans, and it is to this liberation of prussic acid that the numerous cases of poisoning of cattle by Java beans are due. Linseed cake also contains a cyanogenetic glucoside, but the high temperature to which the cake is heated in the course of manufacture destroys the enzyme originally present in the seed, so that on placing the ground cake in water the glucoside is not decomposed, and no prussic acid is liberated.

The seed of the para rubber tree, sometimes used for feeding purposes in the tropics, also yields small quantities of prussic acid.

It is suggested that in estimating the amount of prussic acid obtainable from products of this type analysts should adopt the plan of extracting the whole of the cyanogenetic glucoside from the product under examination by means of a suitable solvent, and then estimate the prussic acid obtained by hydrolysing the extracted glucoside with acids.

NOTICES OF BOOKS.

Dairy Laboratory Guide. By Charles W. Melick, B.S.A., M.S. London: Archibald Constable and Co., Ltd. 1907.

The student who is taking a course of practical dairy work will find this little book very helpful from some points of view. The routine work of a dairy or creamery is described in a series of practical exercises, in which the directions for experimental work are clearly stated, and the student is encouraged to make the greatest possible use of his powers of observation and reasoning. The later part of the book is devoted to the testing of dairy produce for purity and quality. Since the book is intended mainly for students who have time for a short course of laboratory work only, the tests are often mere quick rule-of-thumb methods, and no attempt is made to explain the chemical reactions upon which they are based. None but the simplest processes are included; hence accuracy has had to be sacrificed in some cases, as in the testing of butter for foreign fats. In many respects the book can be regarded only as a satisfactory introductory manual, but its use by the student will save both the time and labour of the dairy instructor who is teaching the making of cheese, butter, &c., to a large class.

Detection of the Common Food Adulterants. By Edwin M. Bruce. London: Archibald Constable and Co., Ltd. 1907.

This little book is one of unquestionable utility. It is devoted exclusively to simple qualitative tests for adulterations in all common articles of food, and it will enable students of chemistry to get useful practice in qualitative analysis, and to become acquainted with the most common adulterants and their detection. The tests are well chosen for simplicity of manipulation and for sensitiveness, and although a great choice of methods is not given, all the commoner adulterants of each substance are taken into consideration. Microscopical work is touched upon, but it is a difficult branch of the subject to learn from any book however excellent, and the absence of illustrations adds to the difficulty. Quantitative tests are not included. The book will be found an excellent introduction to the analysis of foods, and it also provides interesting supplementary work in qualitative analysis.

The Paper-mill Chemist. By Henry P. Stevens, M.A., Ph.D., F.I.C. London: Scott, Greenwood, and Son. 1908.

The chemist employed in paper-mills will never regret adding this volume to his library, but, on the contrary, will probably find that it becomes indispensable to him after a short use. The book treats not so much of the manufacture of paper as of the analysis of the raw materials and finished product, and all tables and analytical data which the analyst is likely to require are arranged in a very convenient form. In the chapter on the detection of adulterations and impurities an account is given of the analysis and valuation of the more important materials used in the manufacture of paper and pulp. The most suitable dyeing materials for colouring pulp, and the best modern methods of applying them, are discussed in much detail, and an illustrated outline of microscope work is included. Methods of performing chemical and physical tests to determine the purity and value of papers are described in clear language which will enable all ordinary analytical operations to be carried out without any possibility of mistake.

Die Englischen Elektrochemischen Patente. ("English Electro-chemical Patents") By Dr. P. Ferchland. Vol. 1. Halle-a-S.: Wilhelm Knapp. 1907.

This is the companion volume to No. XXIV. of the series of Monographs on Applied Electro-chemistry, which treats of the German electro-chemical patents. As English electro-chemical patents date further back than, and far exceed in number, those granted in Germany on the same subject, it has been found necessary to limit the processes included in this volume to those relating to the oldest branch of electro-chemistry (electrolysis), and to reserve for a later volume electrothermic processes. A chronological order has been adopted, and the specifications are so well indexed, both under subjects and patentees' names, that there can be no difficulty in finding any patent, if either its number, inventor's name, or subject is known. A short introduction to the volume gives an outline of the essential points of English patent law, special stress being laid upon the important details in which it differs from German law.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xli., No. 5, 1908.

Liquid Hydrosol of Palladium Hydride.—C. Paal and Josef Gerum.—The authors have found that colloid palladium solutions absorb only insignificant quantities of oxygen from the air. The absorptive power of different colloid palladium solutions for hydrogen varies within wide limits, but no explanation has yet been found for this phenomenon. Liquid palladium hydrosols possess a higher power of absorption for hydrogen than has yet been observed for palladium.

Palladium Hydride.—C. Paal and Josef Gerum.—Palladium black in aqueous suspension takes up much more hydrogen than when the gas is allowed to act upon the solid between $-10°$ and $110°$. The composition of the hydride corresponds almost exactly with the formula PdH.

Determination of Lead, Copper, and Silver in Complicated Organic Salts.—M. Rindl and H. Simonis.—Lead is best determined in its salts of complicated organic acids by evaporation with concentrated sulphuric acid. In compounds containing sulphur in which more than one atom of sulphur is present to one of lead, the determination of lead can be combined with that of the sulphur by Carius's method; the sulphuric acid not combined with the lead is precipitated in the filtrate from the lead sulphate by means of barium chloride. The usual methods of determining copper are very unreliable; evaporation of easily decomposed compounds with concentrated sulphuric acid gives the most satisfactory results. Accurate values are found for silver in compounds containing halogens when the salt is heated in a tube with fuming nitric acid and potassium haloid. Dupont and Freundler's method of evaporation of the substance with aqua regia is quicker.

Classification of Ketenes.—H. Staudinger and H. W. Klever.—Ketenes can be divided into two classes:—(1) Those compounds which do not undergo autoxidation. These are colourless; pyridine and quinoline do not form ketene bases with them, but make them polymerise. To this class belong ketene, methyl ketene, ethyl ketene, and carbon suboxide. (2) The coloured compounds which readily undergo autoxidation. With pyridine and quinoline they form ketene bases, compounds of two molecules of ketene with one of base. Disubstituted ketenes such as diphenyl and dimethyl ketene belong to this class. Both classes readily fix water, alcohol, and amines at the carbon double bond, and form acids and their derivatives. They also fix chlorine and bromine at this double bond. The ketenes of the first-class polymerise very easily. The first-class may be called aldoketenes or aldenes, $\begin{matrix}R\\H\end{matrix}\!>\!C{:}CO$, and the second keto ketenes, $\begin{matrix}R_1\\R_2\end{matrix}\!>\!C{:}CO$.

Refractometer Proof of the Composition of Carbon Suboxide.—Arthur Michael.—Diels and Blumberg have stated that the author's formula for carbon suboxide is probably incorrect, basing their opinion on the results of determinations of the molecular refraction and dispersion of the compound. The author now points out that the optical constants of the acetylene bond vary very considerably, and the optical method does not appear to be trustworthy for distinguishing between the two proposed constitutional formulæ of carbon suboxide. The structure of the oxide can be determined only by experimental methods.

MISCELLANEOUS.

Royal Society of Arts.—It is announced that Mr. William Burton, in consequence of the pressure of other work, is unable to fulfil his engagement to deliver the course of Cantor Lectures on "The Nature and Structure of the Porcelains," announced for Mondays, May 4, 11, and 18. The course will therefore not be given this Session.

The Chemical Laboratory Fresenius at Wiesbaden.—During the Winter Term, 1907-08, the Chemical Laboratory Fresenius was attended by 26 students. Of these, 13 were from Germany, 3 from the United States of America, 2 from Russia, 1 from England, 1 from Belgium, 1 from France, 1 from Holland, 1 from Austria, 1 from Spain, 1 from Argentina, and 1 from East India. There were two assistants in the Instruction Laboratory, and twenty in the private laboratories (Versuchsstationen). To the teaching staff of the institution belong the Directors, Geh. Regierungsrat, Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Heintz, and also Prof. Dr. med. G. Frank, Dr. L. Grünhut, Dr. R. Fresenius, and J. Huber (Architect). The next Summer Term begins on April 24th. From the beginning of next Summer Term ladies are admitted as students. During the Winter Term, 1907-08, besides the scientific researches, a great number of analyses were undertaken in the different departments of the Laboratory (Vessuchsstationen) on behalf of trade, manufacture, mining, agriculture, hygiene, justice, and government.

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THE CENTENARY OF DAVY'S DISCOVERY OF THE METALS OF THE ALKALIS.*

By Prof. T. E. THORPE, C.B., Ph.D., LL.D., D.Sc., F.R.S.

A HUNDRED years ago last October, there happened one of those events to which the term epoch-making may, without cavil or question, be fittingly applied.

As it was an occurrence with which the name and fame of the Royal Institution are inseparably bound up, the Managers have thought it only proper that its centenary should not pass unnoticed here, and it is by their wish therefore that I appear on this the first possible opportunity after the actual date of its hundredth anniversary to give you some account of it, and to state, so far as I am able and within the limits of an hour, the fruitful consequences that have flowed from it.

Let me, in the first place, attempt to recall the circumstances which led up to that cardinal discovery of which to-night we celebrate the centenary. These are connected partly with the Institution itself, and partly with the state of science in the early years of the Nineteenth century.

In the year 1807 this Institution was entering upon the eighth year of its existence. As you doubtless know, the Royal Institution grew out of a proposal to deal with the question of the unemployed—namely, by forming in London by private subscription an establishment for feeding the poor and giving them useful employment, and also for furnishing food at a cheap rate to others who may stand in need of such assistance, connected with an institution for introducing and bringing forward into general use new inventions and improvements, particularly such as relate to the management of heat and the saving of fuel, and to various other mechanical contrivances by which domestic comfort and economy may be promoted. Such was the original prospectus, but like many other prospectuses it failed to equal the promise its projectors held out.

Eventually the promoters decided, on the initiation of Count Rumford, that the Associated Institution would, as they expressed it, be "too conspicuous and too interesting and important, to be made an *appendix* to any other existing establishment," and therefore it ought to stand alone, on its own proper basis.

Accordingly, the problem of the unemployed still remains with us, whilst the new institution took the form of converting Mr. Mellish's house in Albemarle Street into a place where, by regular courses of philosophical lectures and experiments, the applications of the new discoveries in science to the improvement of the arts and manufactures might be taught, so as to facilitate the means of procuring the comforts and conveniences of life.

The Royal Institution had a troubled infancy. Like the poor it was originally designed to succour, it suffered much in the outset from lack of nourishment. To add to its miseries, the little starveling was caricatured by Gillray, lampooned by Peter Pindar, and ridiculed by Lord Brougham; and it was literally in the throes of dissolution when new life was breathed into it by the opportune arrival, in 1801, of a small spare youth of twenty-two, from Bristol, whom the Managers had engaged at a salary of 100 guineas a year. The youth was Humphry Davy, who had acted as assistant to Dr. Beddoes, of the Pneumatic Institution, and who had already made some slight stir in scientific circles by his discovery of a characteristic property of nitrous oxide. In announcing his arrival to the Managers, Count Rumford reported that he had purchased a cheap second-hand carpet for Mr. Davy's room, together with such other articles as appeared to him necessary to make the room habitable, and among the rest a new sofa-bed, which, in order that it may serve as a model for imitation, had been made complete in all its parts. Six weeks after his arrival Davy was called upon to lecture, and a descriptive paragrapher of the period thus chronicles his success in the *Philosophical Magazine* for 1801:—

"It must give pleasure to our readers to learn that this new and useful institution, the object of which is the application of Science to the common purposes of life, may be now considered as settled on a firm basis. . . .

"We have also to notice a course of lectures, just commenced at the institution, on a new branch of philosophy—we mean the Galvanic Phenomena. On this interesting branch, Mr. Davy (late of Bristol) gave the first lecture on the 25th of April. He began with the history of Galvanism, detailed the successive discoveries, and described the different methods of accumulating galvanic influence. . . . . He showed the effect of galvanism on the legs of frogs, and exhibited some interesting experiments on the galvanic effects on the solution of metals in acids. Sir Joseph Banks, Count Rumford, and other distinguished philosophers were present. The audience were highly gratified, and testified their satisfaction by general applause. Mr. Davy, who appears to be very young, acquitted himself admirably well; from the sparkling intelligence of his eye, his animated manner, and the *tout ensemble*, we have no doubt of his attaining a distinguished eminence."

And what was of more immediate consequence, this confident assurance was shared also by the Managers, for at a subsequent meeting they unanimously resolved "that Mr. Humphry Davy, Director of the Chemical Laboratory, having given satisfactory proofs of his talents as a lecturer, should be appointed, and in future denominated, Lecturer in Chemistry at the Royal Institution, instead of continuing to occupy the place of Assistant Lecturer, which he has hitherto filled."

That such shrewd experienced men of the world as Sir Joseph Banks and Rumford, who were the moving spirits in the management of the Institution and genuinely solicitous for its welfare, should thus entrust its fortunes, then at their lowest ebb, to the power and ability of a young and comparatively unknown man, barely out of his teens, seems, even in an age which was familiar with the spectacle of "a proud boy" as a Prime Minister, like the desperate throw of a gambler.

But Banks and Rumford had, doubtless, good reason for the faith that was in them. For a happy combination of circumstances had served to bring the Cornish youth within the range of many who could be of service to him in that search for the fame for which he hungered. His connection with the Beddoes brought him the friendship of the Edgeworths, and it is amusing to trace how the good-humoured patronage of the gifted Maria quickly passed into amazement and ended in awe as her acquaintance with him ripened. Living in Bristol, he was at once brought into that remarkable literary coterie which distinguished that city at the close of the Eighteenth Century. Southey spoke of him as a miraculous young man, whose talents he could only wonder at. Cottle, the publisher, on one occasion said to Coleridge, "You have doubtless seen a great many of what are called the cleverest men—how do you estimate Davy in comparison with these?" Mr. Coleridge's reply was strong and expressive. "Why, Davy can eat them all! There is an energy, an elasticity, in his mind which enables him to seize on and analyse all questions, pushing them them to their legitimate consequences. Every subject in Davy's mind has the principle of vitality. Living thoughts spring up like turf under his feet."

Davy's experimental work on "the pleasure-giving air" had made him known to the Watts and the Wedgewoods. Priestley, then in exile, and Hope, of Edinburgh, were

* A Discourse delivered before the Royal Institution, January 17, 1908.

greatly impressed with the philosophical acumen of the author of phosoxygen, and he had a powerful friend in his own countryman, Davies Gilbert, who succeeded him in the Presidential Chair of the Royal Society. We need be in no doubt, therefore, as to the influences which conspired to bring Davy into what he termed "the great hotbed of human power called London."

The mention of Davy's first course of lectures in this Institution brings me at once to the proper subject of this discourse.

The first year of the last century is memorable for the invention of the voltaic battery, and for its immediate application by Nicholson and Carlisle in this country to the electrolytic decomposition of water.

Davy himself has said, "The voltaic battery was an alarm bell to experimenters in every part of Europe; and it served no less for demonstrating new properties in electricity, and for establishing the laws of this science, than as an instrument of discovery in other branches of knowledge; exhibiting relations between subjects before apparently without connection, and serving as a bond of unity between chemical and physical philosophy."

We owe it to Sir Joseph Banks that Volta's great discovery was first made known to English men of science, and the study of the phenomena of Galvanic Electricity was at once entered upon by a score of experimenters in this country. Among them was Davy. Even before he left Bristol he was hard at work on the subject, sending the results of his observations to *Nicholson's Journal* in a series of short papers. He resumed his inquiries immediately on his arrival in London, and was doubtless well prepared, therefore, for his opening course of lectures.

In 1801 he sent his first communication to the Royal Society on "An Account of some Galvanic Combinations Formed by the Arrangement of Single Metallic Plates and Fluids, Analogous to the New Galvanic Apparatus of Mr. Volta." Although the work was continually interrupted by requests made to him by the Managers to carry out their own ideas of facilitating the means of procuring the comforts and conveniences of life, he never lost sight of the subject of voltaic electricity, and in spite of innumerable distractions due to the precarious position of the Institution, he gradually accumulated the material, out of which grew his first Bakerian Lecture "On some Chemical Agencies of Electricity," read before the Royal Society on November 20th, 1806. I have ventured elsewhere to express my opinion of this paper. In my judgment it constitutes, in reality, Davy's greatest claim as a philosopher to our admiration and gratitude, for in it he, for the first time, succeeded in unravelling the fundamental laws of electro-chemistry, and thereby imported a new order of conceptions, altogether unlooked for and undreamt of, into science.

I am only at the moment concerned with this memoir in its relation to the discovery of which to-night we celebrate the centenary. The isolation of the metals of the alkalis was unquestionably an achievement of the highest brilliancy, and as such appeals strongly to the popular imagination. But it was only the necessary and consequential link in a chain of discovery which, had Davy neglected to make it, would have been immediately forged by another.

The publication of Davy's first Bakerian Lecture produced a great sensation, both at home and abroad. Berzelius, years afterwards, spoke of it as one of the most remarkable memoirs that had ever enriched the theory of chemistry. Very significant, too, of the impression it made on the world of science was the action of the French Institute. Bonaparte, then First Consul, had announced his intention of founding a medal "for the best experiment which should be made in the course of each year on the galvanic fluid," and a committee of the Institute, consisting of Laplace, Halle, Coulomb, Hauy, and Biot, was appointed to consider the best means of giving effect to the wishes of the First Consul. To the young man, with the little brown head, like a boy (as Lady Brownrigg described him), now twenty-eight years of age, was awarded the medal. All the Institute got from the founder of the medal was, what Maria Edgeworth termed, "a rating all round in imperial Billingsgate." There was no *entente cordiale* in those days; indeed, the feeling of animosity was intense. Of course, there were persons who said that patriotism should forbid the acceptance of the award. Davy's own view was more sensible and politic:—"Some people," he said to his friend Poole, "say I ought not to accept this prize; and there have been foolish paragraphs in the papers to that effect; but if the two countries or governments are at war, the men of science are not. That would, indeed, be a civil war of the worst description; we should rather, through the instrumentality of men of science, soften the asperities of national hostility."

Thanks to the kindness of Dr. Humphry Davy, Rolleston, the grandson of Dr. John Davy, the brother of Sir Humphry, who has also been so good as to lend me this admirable bust of the great chemist by Chantrey, and this charming portrait by Jackson, I am able to show you this evening this historically interesting medal.

What Davy looked like at this period of his life may be seen from the picture I now project upon the screen. It is a reproduction of the large portrait which hangs in the vestibule, and which the Institution owes to the thoughtful kindness of the late Mr. Graham Young.

As the applications of voltaic electricity seemed in 1806 to have no immediate bearing on the comforts and conveniences of life, Davy, during the greater part of the following year, was required to direct his attention to other matters. But in the late summer of 1807 he was able to resume his work with the voltaic battery, and he commenced to study its action on the alkalis.

That the alkalis—potash and soda—would turn out to be compound substances was not an unfamiliar idea at the time, and it is significant that almost immediately after Nicholson and Carlisle had resolved water into its elements by the action of voltaic electricity, Henry, of Manchester, the friend and collaborator of Dalton, should have made the attempt to apply the same agency to the separation of the presumed metallic principle of potash. The conception that what the older chemists called "earths" might be made to yield metals was at least as old as the time of Boyle, and probably dates back from the earliest days of alchemy. The relation of the earths to the metals was part of the doctrine of Becher and Stahl; it was no less a part of the antiphologistic doctrine of Lavoisier, although the points of view were diametrically opposed. Neumann attempted to obtain a metal from lime, Bergman considered that baryta was, like lime, a metallic calx, and Baron that alumina contained a metal. From their many analogies to these substances it was not unreasonable, therefore, to surmise that potash and soda might also contain metallic principles.

I have elsewhere pointed out that there is some evidence that whilst at Bristol Davy had already attacked the problem of the resolution of the alkalis by means of voltaic electricity. What precise idea he had in again attacking it, or what expectation he had of a definite result, is difficult to determine. In one of his lectures on Electro-chemical Science, delivered some time subsequently, he said he had a suspicion at the time that potash might turn out to be "phosphorus or sulphur united to nitrogen," conceiving, that as the volatile alkali was composed of the light inflammable hydrogen united to nitrogen, so the fixed and denser alkalis might be composed of the denser inflammable bodies—phosphorus and sulphur—also united to nitrogen.

Davy once said that "analogy was the fruitful parent of error," and few more striking instances of perverted analogy are to be met with in science than this. In another of his lectures he said of the alchemists that "even their *failures* developed some unsought-for object partaking of the marvellous"; and if such had been his reasoning, the statement is no less true of himself.

So far as can be ascertained, it was on October 19, 1807, that he obtained his first decisive result. This is thus

described in Davy's own handwriting in the Laboratory Journal, which has been preserved for us by the pious care of Faraday, and which is one of the most precious of the historical possessions of the Royal Institution:—"When potash was introduced into a tube having a platinum wire attached to it, so [fig.], and fused into the tube so as to be a conductor—*i.e.*, so as to contain just water enough, though solid—and inserted over mercury, when the platina was made negative, no gas was formed, and the mercury became oxydated, and a small quantity of the alkaligen was produced round the platina wire, as was evident from its quick inflammation by the action of water. When the mercury was made the negative, gas was developed in great quantities from the positive wire, and none from the negative mercury, and this gas proved to be pure oxygen —a capital experiment, proving the decomposition of potash."

On the 19th of the following month he delivered what is generally regarded as the most memorable of all his Bakerian Lectures. It is entitled "On some New Phenomena of Chemical Changes produced by Electricity, particularly the Decomposition of the fixed Alkalis; and the Exhibition of the New Substances which Constitute their Bases; and on the General Nature of Alkaline Bodies."

Few discoveries of like magnitude have been made and perfected in so short a time, and few memoirs have been more momentous in result than that which, put together in a few hours, gave the results of that discovery to the world.

The whole work was done under conditions of great mental excitement. His cousin, Edmund Davy, who at the time acted as his assistant, relates that when he saw the minute globules of the quicksilver-like metal burst through the crust of potash and take fire, his joy knew no bounds; he actually danced about the room in ecstasy, and it was some time before he was sufficiently composed to continue his experiments.

The rapidity with which he accumulated results, after this first feeling of delirious delight had passed, was extraordinary, and he had obtained most of the leading facts concerning the physics and chemistry of the new substances before the middle of November.

He began his lecture with a felicitous reference to the concluding remarks of one of the previous year, namely:—"That the new methods of investigation promised to lead to a more intimate knowledge than had hitherto been obtained concerning the true elements of bodies. This conjecture, then sanctioned only by strong analogies, I am now happy to be able to support by some conclusive facts."

In the first attempts he made to decompose the fixed alkalis he acted upon concentrated aqueous solutions of potash and soda with the highest electrical power he could then command at the Royal Institution, viz., from voltaic batteries containing 23 plates of copper and zinc of 12 inches square, 100 plates of 6 inches, and 150 of 4 inches, charged with solutions of alum and nitric acid; but although there was high intensity of action, nothing but hydrogen and oxygen was disengaged. He next tried potash in igneous fusion, and here the results were more encouraging; there were obvious and striking signs of decomposition; combustible matter was produced, accompanied with flame and a most intense light. He had observed that, although potash, when dry, is a non-conductor, it readily conducts when it becomes damp by exposure to air, and in this state "fuses and decomposes by strong electrical powers."

Let me state in his own words, for the words are classical, what followed:—

"A small piece of pure potash, which had been exposed for a few seconds to the atmosphere, so as to give conductive power to the surface, was placed upon an insulated disc of platina, connected with the negative side of the battery of the power of 250 of 6 and 4 [that is 100 plates of 6 inches square and 150 plates of 4 inches square] in a state of intense activity: and a platina wire communicating with the positive side was brought in contact with the upper surface of the alkali. . . . Under these circumstances a vivid action was soon observed to take place. The potash began to fuse at both its points of electrization. There was a violent effervescence at the upper surface; at the lower or negative surface, there was no liberation of elastic fluid; but small globules, having a high metallic lustre, and being precisely similar in visible characters to quicksilver, appeared, some of which burnt with explosion and bright flame, as soon as they were formed, and others remained, and were merely tarnished, and finally covered by a white film which formed on their surfaces."

He goes on to say:—

"Soda, when acted upon in the same manner as potash, exhibited an analogous result; but the decomposition demanded greater intensity of action in the batteries, or the alkali was required to be in much thinner and smaller pieces.

"The substance produced from potash remained fluid at the temperature of the atmosphere at the time of its production; that from soda, which was fluid in the degree of heat of the alkali during its formation, became solid on cooling, and appeared having the lustre of silver."

It would seem from this description of its properties that the potassium Davy first obtained was alloyed with sodium owing to the fact that the potash contained soda. Potassium is solid up to 143° F., whereas, as Davy was the first to show, an alloy of potassium and sodium is fluid at ordinary temperatures.

On account of their alterability in contact with air, Davy had considerable difficulty in preserving and confining the new substances so as to examine their properties. As he says, like the Alkahests imagined by the Alchemists, they acted more or less upon almost every body to which they were exposed. Eventually, he found they might be preserved in mineral naphtha.

The "basis" of potash were described by him as a soft malleable solid with the lustre of polished silver.

"At about the freezing-point of water it becomes harder and brittle, and when broken in fragments exhibits a crystallised texture which in the microscope seems composed of beautiful facets of a perfect whiteness and high metallic splendour. It may be converted into vapour below a red heat, and may be distilled unchanged, and is a perfect conductor of heat and electricity. Its most marked difference from the common run of metals is its extraordinary low specific gravity." At the time of its discovery it was the lightest solid known.

The "basis" of soda was found to have somewhat similar properties. It was slightly heavier than the "basis" of potash, and fused at a higher temperature.

Davy next examined the behaviour of the new substances towards a large number of reagents, but as his observations are now the common property of the text-books, it is unnecessary here to dwell upon them.

He then enters upon some general observations on the relations of the "bases" of potash and soda to other bodies:—

"Should the bases of potash and soda be called metals? The greater number of philosophical persons," he says, "to whom this question has been put, have answered in the affirmative. They agree with metals in opacity, lustre, malleability, conducting powers as to heat and electricity, and in their qualities of chemical combination.

"Their low specific gravity does not appear a sufficient reason for making them a new class; for amongst the metals themselves there are remarkable differences in this respect. . . . In the philosophical division of the classes of bodies, the analogy between the greater number of properties must always be the foundation of arrangement.

"On this idea, in naming the bases of potash and soda, it will be proper to adopt the termination which by common consent has been applied to other newly discovered metals, and which, though originally Latin, is now naturalised in our language.

"Potasium (*sic*) and sodium are the names by which I have ventured to call the new substances; and whatever changes of theory, with regard to the composition of bodies, may hereafter take place, these terms can scarcely express an error; for they may be considered as implying simply the metals produced from potash and soda. I have consulted with many of the most eminent scientific persons in this country upon the methods of derivation, and the one I have adopted has been the one most generally approved. It is perhaps more significant than elegant. But it was not possible to found names upon specific properties not common to both, and though a name for the basis of soda might have been borrowed from the Greek, yet an analogous one could not have been applied to that of potash, for the ancients do not seem to have distinguished between the two alkalies."

Such, then, are the more significant features of one of the greatest discoveries ever made by a British chemist, as these are set forth in one of the most remarkable papers in the *Philosophical Transactions of the Royal Society*.

(To be continued).

EXPLOSIVE COMBUSTION, WITH SPECIAL REFERENCE TO THAT OF HYDROCARBONS.*

By Professor WILLIAM ARTHUR BONE, D.Sc., Ph.D., F.R.S.

It is hardly necessary to remind you that the subject of my discourse will be ever associated with the illustrious name of Davy. Davy turned his attention to the phenomena of flame in the year 1815, in response to an urgent appeal on the part of a committee formed in the North of England, to investigate the causes of accidents arising from the explosion of fire-damp in coal mines, and to devise means for their prevention. The perennial interest of his researches, however, lies not so much in their immediate practical success, great as this undoubtedly was, as in the broader theoretical issues which were disclosed, and brought within the region of experimental enquiry, by so splendid an exercise of genius.

Davy insisted on the necessity of considering flames in all cases "As the combustion of an *explosive mixture* of inflammable gas, or vapour, and air," and he defined flame as "aëriform, or gaseous matter, heated to such a degree as to be luminous." For the starting and propagation of a flame in an explosive mixture, he showed that each successive layer of gas must be raised to a certain definite temperature, called the "ignition point," and he investigated both the ignition temperatures and the explosion limits of a large number of the commoner combustible gases. He then proceeded to his famous discovery that, notwithstanding the extremely high temperatures of flames, which, in the case of cyanogen, he estimated to be "above 5000° of Fahrenheit," they can be readily extinguished by contact with a cooling surface of sufficient area and heat conducting power, and that for this purpose metal surfaces are by far the most efficient. How he developed and applied this discovery to the construction of his "safe-lamp" for miners is, of course, a matter of history.

In experimenting upon the ignition temperatures of explosive mixtures, Davy made the important and far-reaching discovery that combustible gases combine with oxygen at lower temperatures without any appearance of flame whatever. He emphasised the importance of a complete investigation of the chemical aspects of this flameless combustion, and he himself was led to ask whether, seeing that the temperatures of flames far exceed those at which solids become incandescent, a metallic wire can be raised to incandescence by the slow combustion of two gases "without actual flame, but producing heat enough to keep the wire ignited." In this way he discovered the remarkable property of platinum and other metallic wires of inducing surface combustion, and in the course of his further experiments on this subject, he made two notable observations respecting the burning of compounds containing carbon and hydrogen. He found "much carbonic oxide" produced when a platinum wire was kept incandescent by the slow combustion of a mixture of ethylene and oxygen, rendered non-explosive by an excess of the hydrocarbon, and in a similar experiment with ether vapour, he recorded the appearance of "a pale phosphorescent light" accompanied by "the formation of a peculiar acrid volatile substance possessed of acid properties."

Finally, in speculating upon the difficult and thorny subject of the luminosity of hydrocarbon flames, he was "led to imagine" that it "might be owing to the *decomposition* of part of the gas towards the interior of the flame where the air was in smallest quantity, and the deposition of solid charcoal, which, first by its *ignition*, and afterwards by its *combustion*, increased in a high degree the intensity of the light." It is important to observe that not only did Davy rightly attribute the luminosity of a hydrocarbon flame to the presence therein of incandescent carbon, but also that he avoided the error of attributing the separation of carbon to a supposed preferential burning of hydrogen.

In considering the propagation of a flame through an explosive mixture of gases, it is necessary to distinguish between two well-defined conditions. When such a mixture is ignited, the flame travels for a certain limited distance (a few feet only) at a fairly uniform slow velocity, which in the case of a mixture of hydrogen and oxygen in their combining ratios is approximately thirty-four metres (thirty-eight yards) per second. This initial stage of the combustion is called "*inflammation*."

After traversing a few feet, however, the flame begins to vibrate, and alters in character. The vibrations become more and more intense, the flame swinging backwards and forwards with oscillations of increasing amplitude. Then one or other of two things happens; either the flame is extinguished, or it goes forward with an exceedingly great and constant velocity, producing the most violent effects. The new condition thus set up is termed "*Detonation*," and the forward movement of the flame is called the "*Explosion Wave*."

The discovery of "*detonation*" in gaseous mixtures was made simultaneously by M. Berthelot and MM. Mallard and Le Chatelier, in the year 1881; Berthelot proved that the velocity of the explosion wave is independent of the length of the column of gas traversed, and that for the same gaseous mixture under given physical conditions it always has a constant value. In this connection I would mention Prof. H. B. Dixon's exhaustive researches on the "*rates of explosion*" of gaseous mixtures, which have extended in so many ways our knowledge of explosive combustion.

Experiment I.

Perhaps the best illustration of the outward difference between ordinary "*inflammation*" and "*detonation*" is afforded by the case of a mixture of carbonic oxide and oxygen in their combining ratios. When ignited in an open tube four or five inches long, the mixture burns quietly with the familiar blue flame. Far otherwise is it, however, when a long column of the mixture is fired in a leaden coil, where the brief initial period of *inflammation* is succeeded by the *explosion wave*, which dashes onwards through the gases at a rate of 1700 metres (about a mile) per second with shattering effect.

Another notable feature of "*detonation*" is the extremely short duration of the flame. In the course of some experiments carried out under Prof. Dixon's direction, it was found that the duration of luminosity in each successive layer of gas in the detonation of electrolytic gas does not exceed 1 5000th part of a second. But short as this time is, it is something like a million times longer than the

* Discourse delivered before the Royal Institution, February 28, 1908.

interval between successive molecular collisions in a gaseous mixture.

The question of how a hydrocarbon burns, that is to say, precisely how it is attacked by the oxygen, has been the subject of much discussion during the past fifteen years. A hydrocarbon is a compound of the two combustible elements, carbon and hydrogen, and in a sufficient supply of oxygen, both of these are ultimately burnt to carbon dioxide and steam, respectively. Thus, for example, in the case of ethane :—

$$\underset{2\text{ vols.}}{2C_2H_6} + \underset{7\text{ vols.}}{7O_2} = \underset{4\text{ vols.}}{4CO_2} + \underset{6\text{ vols.}}{6H_2O}.$$

On kinetic grounds, however, it seems inconceivable that the passage from the initial system of ethane and oxygen to the final system of carbon dioxide and steam can be immediate and direct. It is, therefore, universally recognised that the process involves a number of successive stages. But opinion has been sharply divided as to the nature and sequence of these stages, and I will now endeavour to put before you the main points in dispute. They may be conveniently summarised under three heads.

1. During the greater part of last century the belief prevailed that the hydrogen is much the more combustible of the two elements of a hydrocarbon, and that consequently when combustion occurs in a limited supply of oxygen, the hydrogen is preferentially burnt, as follows :—

$$C_2H_4 + O_2 = 2C + 2H_2O.$$

Who was the author of this view, or what was originally its experimental basis, is not quite clear, but it received the active support of two such eminent authorities as Thomas Graham and Michael Faraday, and for fifty years it was regarded as one of the most certain articles of chemical faith. Its final overthrow by Dixon and Smithells in the year 1892 caused no small stir in chemical circles.

2. The second theory originated with Kersten in 1861, who as the outcome of experiments on the explosion of a mixture of ethylene and electrolytic gas, asserted that "before any portion of the hydrogen is burnt, all the carbon is burnt to carbonic oxide, and that the excess of oxygen then divides itself between the carbonic oxide and the hydrogen." In other words, Kersten attempted to substitute the idea of the preferential burning of carbon for that of the preferential burning of hydrogen. His views, however, received no serious attention until they were revived and endorsed by Dixon and Smithells in 1892.

The chief experimental basis for this theory is the behaviour of ethylene and acetylene when exploded with their own volume of oxygen. More than a century ago, Dalton found that a mixture of equal volumes of ethylene and oxygen yields mainly carbonic oxide and hydrogen on explosion, without any separation of carbon, in conformity with the equation :—

$$\underset{1\text{ vol.}}{C_2H_4} + \underset{1\text{ vol.}}{O_2} = \underset{2\text{ vols.}}{2CO} + \underset{2\text{ vols.}}{2H_2}.$$

This fact, after being overlooked for nearly eighty years, was re-discovered by Dixon in 1891 ; moreover, a few years later, when it was proved that acetylene behaves in a precisely similar manner :—

$$\underset{1\text{ vol.}}{C_2H_2} + \underset{1\text{ vol.}}{O_2} = \underset{2\text{ vols.}}{2CO} + \underset{1\text{ vol.}}{H_2},$$

the advocates of the theory were able to claim a strong body of evidence in support of their case.

3. But the idea of a "*preferential*" combustion, whether of carbon or of hydrogen, seemed repugnant to well-established principles concerning the nature and conditions of chemical interactions in gaseous systems. Moreover, whilst the assumption of a *direct* passage from an initial system of ethylene and oxygen, $C_2H_4 + O_2$, to the system carbonic oxide and hydrogen, $2CO + 2H_2$, implied a simple transaction from the kinetic standpoint, an extension of the idea to the case of such a hydrocarbon as propylene—

$$2C_3H_6 + 3O_2 = 6CO + 6H_2,$$

would at once raise serious difficulties.

It therefore remained to consider whether the solution of the problem might not lie in the assumption of an initial *association* of the hydrocarbon and oxygen forming an unstable "oxygenated" molecule, which subsequently rapidly decomposes. Thus, for example, the changes involved in the explosive combustion of an equimolecular mixture of ethylene and oxygen might conceivably be represented somewhat as follows :—

$$C_2H_4 + O_2 = \underset{\text{Unstable.}}{[C_2H_4O_2]} = 2CO + 2H_2.$$

Many years ago, indeed, Prof. H. E. Armstrong suggested that the combustion of a hydrocarbon takes place under the conjoint influence of water and oxygen, and involves the successive formation of intermediate "*hydroxylated*" molecules, which at high temperatures rapidly decompose into simpler products. Little notice was taken of his suggestion at the time, but recent researches have shown that "*hydroxylated*" molecules are probably formed, even in flames, although I think it doubtful whether water vapour is an essential factor in the process.

The researches recently carried out at the Manchester University have covered the entire range of conditions under which hydrocarbons can be burned, from the slow flameless combustion discovered by Davy, right up to the extreme conditions of detonation. An exhaustive study of the slow combustion of methane, ethane, ethylene, and acetylene, at temperatures between 250° and 400° C., afforded decisive evidence against the preferential burning, whether of carbon or of hydrogen. Large quantities of aldehydic intermediate products were isolated, and the balance of evidence was decidedly in favour of the "*hydroxylation*" theory, with the proviso, however, that the oxygen is directly active. Finally, the following scheme was put forward for the slow combustion of ethane, and ethylene at 250° to 350° C. :—

$$\underset{\text{Ethane}}{CH_3.CH_3} \rightarrow \underset{\text{Ethyl alcohol}}{CH_3.CH_2OH} \rightarrow \overbrace{CH_3.CH(OH)_2}^{H_2O + CH_3.CHO\text{—Acetaldehyde}} \rightarrow CO + H_2O + \underset{\text{Formaldehyde}}{H.CHO} \rightarrow \overbrace{H.COOH}^{\text{Formic acid}} \rightarrow \overbrace{CO(OH)_2}^{\text{Carbonic acid}}$$

$$\overbrace{CO + H_2O}^{\text{Formic acid}} \qquad \overbrace{CO_2 + H_2O}^{\text{Carbonic acid}}.$$

$$\underset{\text{Ethylene}}{CH_2{:}CH_2.} \rightarrow H_2C{:}CH(OH) \rightarrow \overbrace{(HO)CH{:}CH(OH)}^{2H.CHO\text{—Formaldehyde}} \rightarrow \overbrace{H.COOH}^{\text{Formic acid}} \rightarrow \overbrace{CO(OH)_2}^{\text{Carbonic acid}}$$

$$\overbrace{CO + H_2O}^{\text{Formic acid}} \qquad \overbrace{CO_2 + H_2O}^{\text{Carbonic acid}}$$

Translated into words, this means that, in the case of ethane, the initial oxidation product is probably *ethyl alcohol* $C_2H_5.OH$. The alcohol has not, indeed, been actually isolated during the slow combustion at 300° C., chiefly because it is much more rapidly oxidised under these conditions than is ethane itself; it is, however, formed in quantity when ethane is oxidised by means of ozone at 100° C. The second stage involves the rapid oxidation of the alcohol to the unstable $CH_3.CH(OH)_2$, which at once decomposes into steam and *acetaldehyde*. The acetaldehyde is in turn burnt to carbonic oxide, steam, and *formaldehyde* $\left(\text{possibly through the unstable } \begin{matrix} .H \\ HO.C.H \\ HO{\cdot}\dot{C}{:}O \end{matrix}\right)$, and finally the formaldehyde is burnt to steam and oxides of carbon, probably through *formic acid* and *carbonic acid*.

As the temperature rises, the intermediate products become more and more unstable, and to an increasing extent decompose into simpler products, which then undergo independent oxidation. Thus *ethyl alcohol* decomposes into ethylene and steam, *acetaldehyde* either into methane and carbon monoxide, or into carbon, hydrogen,

methane, and carbon monoxide, according to the temperature, and *formaldehyde* is resolved into carbon monoxide and hydrogen, as follows:—

Ethyl Alcohol.	Acetaldehyde.	Formaldehyde.
C_2H_5OH.	$CH_3.CHO$	$H.CHO$
$C_2H_4+H_2O$.	$\begin{cases} CH_4+CO \\ C+2H_2+CO \end{cases}$	$CO+H_2$

With the extension of the research to the conditions existing in hydrocarbon flames and explosions, it became increasingly evident that the mechanism of combustion is essentially the same above as below the ignition point. I do not mean, of course, that the phenomena observed at low temperatures, in slow combustion, are exactly reproduced in flames, but rather that the result of the initial molecular encounter between the hydrocarbon and oxygen is probably much the same in the two cases, namely, the formation of an "oxygenated" molecule. At the higher temperatures of flames, secondary thermal decompositions undoubtedly come into operation at an earlier stage, and play a more important *rôle* than in slow combustion, but they do not precede the onslaught of the oxygen upon the hydrocarbon, but arise in consequence of it. I am aware that there are eminent critics who, whilst admitting the validity of these views as applied to slow combustion, hesitate to accept entirely their extension to explosive combustion. They find it difficult to believe that such compounds as ethyl alcohol, acetaldehyde, formaldehyde, and the like, which are undoubtedly very unstable at high temperatures, can possibly be formed in flames. But surely this objection involves some confusion of thought as to the factors which govern the formation and stability of chemical compounds; the fact that a substance cannot permanently exist at a given temperature does not justify the assertion that it cannot be formed at that temperature by the operation of factors which are not concerned in its decomposition. Therefore, I am not prepared to admit that because the acetaldehyde molecule does not long remain intact at high temperatures, it necessarily follows that it cannot be brought into actual existence as the result of the interaction of ethane and oxygen in flames.

Professor Smithells, in his recent presidential address to the Chemical Section at the British Association (1907), expressed his dissent from my views, as applied to flames, on the ground that "The isolation of an intermediate product under one set of circumstances is in itself no proof that this product is transitorily formed when the reaction is proceeding under another set of circumstances. . . ." To this I would reply, that whilst the isolation of (say) acetaldehyde in the slow oxidation of ethane is not *by itself* sufficient proof of its transitory formation in the explosive combustion of the hydrocarbon, yet if it can be demonstrated, not only that the facts of explosive combustion can be *best* interpreted on the assumption of its formation, but that, so far as can be judged at present, no other interpretation can be advanced, and, moreover, that aldehydes are actually produced in flames, then it may be justly claimed that the assumption is well founded, and that the onus of its experimental disproof rests with the sceptics. (To be continued).

APPARATUS FOR SUBLIMATION.

By W. G. LLEWELLYN.

Purification of a substance by sublimation is very easily and rapidly carried out in the apparatus here described.

It consists of an open tube about five and a-half inches long fitting closely inside a six-inch test-tube. The open tube is conveniently made from a large test-tube by cutting the closed end off.

The substance to be sublimed is placed in the test-tube, warmed, and condensed on the inner tube. This is removed, scraped, and the substance obtained free from any charred residues.

A plug of glass-wool fitting loosely into the open end of he apparatus prevents the escape of vapour.

MARIGNACITE.*

A New Variety of Pyrochlore from Wausau, Wisconsin.

By S. WEIDMAN and VICTOR LENHER.

In the north-central part of Wisconsin, within the general pre-Cambrian area, there are widespread occurrences of igneous rocks intrusive in the Huronian sedimentaries. ("Geology of North Central Wisconsin," *Bull.* No. xvi., Wisconsin Geological and Natural History Survey). Chief among these intrusives is a complex magma, consisting of various phases of granite, quartz-syenite and nepheline-syenite. Pegmatitic modifications are a characteristic feature of the granite-syenite magma, both nepheline and quartz-bearing pegmatites being developed in considerable quantity. In several phases of the quartz-bearing pegmatite a small octahedral mineral was observed that proved upon investigation to be a variety of the rare group of pyrochlore minerals, the principal constituents of which are the metals of the rare earths.

The minerals associated with the pyrochlore in the pegmatite consist mainly of quartz, alkali-felspar, and acmite. Other minerals in the pegmatite veins of the locality are lithia-mica, lepidomelane, varieties of acmite-pyroxene high in alumina and potassium, rutile, fluorite, and several zirconium-bearing minerals. The pegmatite and associated-granite and syenite are closely related in composition, and are characterised by a relatively high content of alumina and soda. In most respects the granite and nepheline-syenite are similar to the well-known occurrences of nepheline-bearing and associated rocks of Arkansas, Ontario, Canada, Essex County, Mass., and the Christiania region of southern Norway.

The pyrochlore was found in the pegmatite occurring along the road in the S.W. 1/4 of Sec. 22, T. 29, R. 6 E., about nine miles north-west of Wausau. It occurs only in small crystals of nearly perfect octahedral form, varying in form up to about one-eighth inch (3 mm.) in diameter. The mineral was found in small quantity, and although after its identification further search was made for it, only a small additional amount was secured. It is likely, however, that the pyrochlore will be found elsewhere in the pegmatite veins of the immediate locality, although very probably only in small quantity.

The only form of the mineral observed was the simple octahedron (Fig. 1). Some of the crystals occur in aggregates (Figs. 2 and 3) and some show a slightly distorted form, but no combinations with other crystal forms were observed. Under the microscope inclusions of quartz and felspar were seen. This examination showed the mineral to be homogeneous, with none of the characteristic features of alteration or of replacement.

Chemical Analysis.—The pyrochlore used for analysis was first picked out by hand from the crushed rock. As the latter was somewhat disintegrated, many of the small octahedral crystals were readily separated from the associated minerals by crumbling the rock under pressure of the hand. Before the mineral was powdered each crystal was examined with a hand lens and all adhering minerals were rubbed off so far as possible. After being powdered and passed through a 100-mesh sieve, the powdered material was subjected to separation by a specific gravity solution of silver-thallium nitrate, and by this method the adhering and included particles of quartz, felspar, and acmite were separated from the pyrochlore. The relatively high specific gravity of the pyrochlore furnished conditions favourable for the separation by the specific gravity method, and for this reason, as well as others later described, the mineral analysed is believed to have been essentially pure.

The analysis of the pyrochlore made upon 3·15 grms., and the molecular ratio of the constituents, is as follows:—

* Published by permission of the Director of the Wisconsin Geological and Natural History Survey. From the *American Journal of Science*, xxiii, p. 267.

Analysis of Pyrochlore (Marignacite) from Wausau, Wisconsin.

	Analysis.	Molecular Ratio.
Cb_2O_5	55·22	0·198
Ta_2O_5	5·86	0·013
SiO_2	3·10	0·051
TiO_2	2·88	0·036
Fe_2O_3	0·50	0·003
FeO	0·02	
Ce_2O_3	13·33	0·040
Yt_2O_3	5·07	0·022
ThO_2	0·20	0·001
CaO	4·10	0·073
MgO	0·16	0·004
Na_2O	2·52	0·041
K_2O	0·57	0·006
F	none	———
H_2O at 110°+	5·95	0·331
H_2O at 110°−	0·45	
	99·93	

Al_2O_3, MnO, SnO_2, WO_3, Di_2O_3, La_2O_3, Er_2O_3, occur in traces, while F, ZrO_2, BeO, UO_2, Li_2O, could not be detected. The mineral shows no radio-activity.

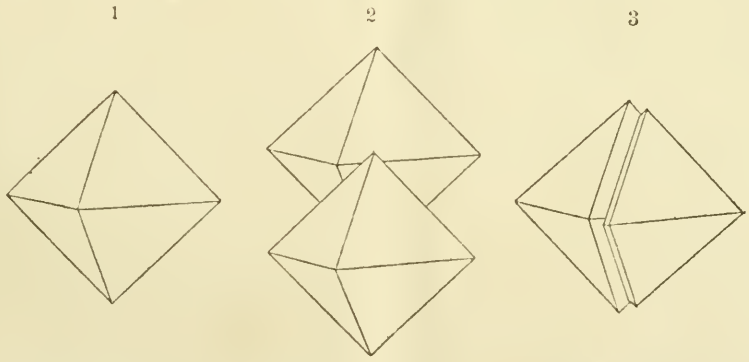
The mineral has a hardness of 5 to 5·5, a specific gravity of 4·13. The cleavage is indistinct, the mineral is brittle and breaks with a conchoidal fracture. The lustre is resinous on fractured surfaces. The streak is light brown to yellowish-brown. The colour varies from a light to dark brown in the hand specimen, while under the microscope a yellow brown to red brown is shown.

It is sub-translucent to transparent. The index of refraction is relatively high and anomalous double refraction is characteristic. Before the blowpipe it is infusible and unchanged. In the borax or salt of phosphorus bead, it dissolves with a yellow colour while hot, and is colourless when cold. The mineral is very refractory to the acids, and is only slightly attacked by fused sodium carbonate. It is attacked in the cold by hydrofluoric acid, and can be decomposed by fusion with either potassium acid sulphate or potassium acid fluoride.

For analysis the mineral can be decomposed either by fusion with potassium acid sulphate, in which case the silica and metallic acids can be separated from the earths, &c., or it can be decomposed by treatment with hydrofluoric acid, when the metallic acids pass into solution, leaving the earthy fluorides insoluble.

Silica was estimated in the residue obtained from repeated extractions of a bisulphate fusion by volatilisation with hydrofluoric acid in the presence of sulphuric acid. The columbic and tantalic acids were tested for tin, molybdenum, tungsten, titanium, and the earths. The titanium was separated from them by a bisulphate fusion, and the metallic acids were separated by the Marignac method of crystallising the double potassium fluorides from each other. It is perfectly well appreciated that the results for columbium and titanium are only closely approximate, for as shown by Hall (*Journ. Am. Chem. Soc.*, xxvi., 1235), Smith (*Ibid.*, xxvii., 1369), and Warren (*Am. Journ. Sci.*, 1906, xxii., 520), it is impossible by present methods to obtain a perfect separation of these two elements. Six crystallisations were made to separate the columbium and tantalum.

The earths after being precipitated together were treated in acid solution with ammonium oxalate. The oxalates were ignited, dissolved in nitric acid, and the excess of acid removed by evaporation. The nitrates were treated with a saturated solution of potassium sulphate. The thoria was separated by means of the thiosulphate and ammonium oxalate methods. The ceria was purified by suspending the hydrate in a solution of potassium hydroxide and treating with chlorine. The weighed oxide was of a salmon colour, and when dissolved as nitrate its solution showed no absorption bands. Didymium and lanthanum could be detected only in traces. In the soluble yttrium group the nitrate solution showed the erbium bands quite markedly. Fluorine, zirconium, beryllium, uranium, and lithium were carefully tested for, but found to be absent. The basic portion of this mineral is largely composed of the cerium and yttrium metals, while silica and the oxide of titanium appear to the extent of nearly 6 per cent. From the careful manner with which the mineral used for analysis was selected and purified, and from the microscopic character of the fragments used, it appears as though the silica and titanium oxide were normal constituents of the mineral.



Fluorine could not be detected by even the most careful examination. The high content of water, 5·95 per cent, given off above 110 degrees and the absence of fluorine may be due to the fact that fluorine and hydroxyl are mutually interchangeable in this group of minerals, as they are in the lithia fluorine micas, and in triploidite and related minerals of the wagnerite group. The isomorphism between hydroxyl and fluorine was first demonstrated by the late Prof. Penfield, who showed its existence for the first time in triploidite, and later in many other minerals in which these radicals occur.

The analyses of marignacite and the several members of the pyrochlore group given in the table show the presence of either or both of these radicals in each of the completed analyses. While a careful determination of the hydroxyl in the analyses of these minerals has apparently not been carried out, it seems reasonable to apply the principle of isomorphism of these radicals in this group.

The presence of an appreciable content of silica, 3·10 per cent, in the pyrochlore from Wausau, perhaps needs further discussion. As already stated, the pyrochlore is associated in the rock with quartz, felspar, and varieties of aluminous acmite containing 5 per cent Al_2O_3 and above, and these minerals to a slight extent were necessarily included in the powdered material prepared for the

specific gravity separation. Previous to powdering the material, however, each pyrochlore crystal was examined and all material clinging to the latter was rubbed off so far as possible. The relatively high specific gravity of the pyrochlore, namely, 4·13 as compared with 2·6 of quartz, 2·6 of felspar, and 3·5 of acmite, should furnish a favourable means for separation by the method adopted. The fact that the chemical analysis shows only a trace of alumina indicates the essential absence of felspar and aluminous pyroxene in the material analysed. And if these minerals were successfully removed from the powdered material in the process of separation by the specific gravity method, it seems reasonable to believe also that the quartz was removed at the same time and to the same extent. Hence it seems probable that the silica is a normal constituent of this mineral.

If the SiO_2 is an original constituent of this pyrochlore, it differs in this respect from other varieties of pyrochlore. Silica is shown in the analysis of some of the members of the columbate-tantalate groups, but it is usually considered of secondary origin. However, if the silica with the titanium oxide are normal constituents, they indicate an interesting relation in the composition of this pyrochlore to many of the titano-silicate minerals, such as tscheffkinite, johnstrupite, mosandrite, rinkite, and also to dysanalyte. In content of cerium oxide this pyrochlore from Wausau is higher than in any of the other pyrochlores, and in its high content of cerium oxide it also resembles the titano-silicates referred to. This pyrochlore with appreciable content of SiO_2, believed to be a normal constituent, therefore, shows an interesting relation in composition between the titano-silicates on the one hand and of the columbate-tantalates on the other.

In the table the analysis of the pyrochlore from Wausau is shown in comparison with the analyses of the typical varieties described by various investigators. By comparison of the several analyses in the table it may be seen that the pyrochlore from Wausau differs from the others in the proportion of each of the several acid and basic radicals. The principal difference in composition with respect to individual constituents appears to be the relatively higher content in the Wausau pyrochlore of cerium and yttrium, and the lower content of lime and iron as compared with the other members of the pyrochlore group. The presence of silica in the Wausau pyrochlore is also a distinctive feature, as already stated.

The name *marignacite* is proposed for this variety of pyrochlore in honour of Marignac, who besides making other valuable contributions to chemistry, developed the method for separating columbium and tantalum through the agency of the difference of solubility of their double fluorides in hydrofluoric acid, which is to-day the most satisfactory method of separating these two elements.

Analyses of Varieties of Pyrochlore.

1. Pyrochlore from Brevik, Norway: Analyst, C. F. Rammelsberg; cited by Brögger, *Zeit. Kryst.*, xvi., p. 512.
2. Koppite, from Schelingen, Baden: G. H. Bailey, *Journ. Chem. Soc.*, 1886, xlix., p. 153.
3. Marignacite from Wausau, Wisconsin: Analyst, V. Lenher, 1906.
4. Hatchettolite from Mitchell Co., N. Carolina: O. D. Allen, *Am. Journ. Sci.*, 1877, xiv., p. 128.
5. Pyrochlore from Batum: G. P. Tschernik, *Zeit. Kryst.*, 1904, xxxix., 624.
6. Microlite, Amelia Court House, Virginia: Dunnington, *Am. Chem. Journ.*, 1881, iii., p. 130.

	1.	2.	3.	4.	5.	6.
Cb_2O_5	58·27	61·64	55·22	34·24	26·22	7·74
Ta_2O_5	—	—	5·86	29·83	27·39	68·43
TiO_2	5·38	0·52	2·88	1·61	4·20	—
SiO_2	—	—	3·10	—	—	—
Fe_2O_3	—	—	0·50	—	0·26	0·42*c*
FeO	—	3·01	0·02	2·19	6·32	—
CaO	10·93	16·61	4·10	8·87	6·00	11·80
MgO	—	1·62	0·16	0·15	—	1·01
Na_2O	5·31	3·58*f*	2·52	1·37	3·15	3·15*d*
K_2O	—	0·36*g*	0·57	Trace	—	—
ThO_2	4·96	—	0·20	—	—	—
Ce_2O_3	5·50	6·89*b*	13·33	—	12·34	0·17*e*
Yt_2O_3	—	—	5·07	—	—	0·23
Di_2O_3	—	—	—	—	0·63	—
La_2O_3	—	—	—	—	0·71	—
UO_2	5·53*a*	—	None	15·50	8·33	1·59
SnO_2	—	—	Trace	0·30	—	1·05
WO_3	—	—	Trace	—	—	0·30
BeO	—	—	—	—	—	0·34
ZrO_2	—	3·39	None	—	—	—
F	3·75	Trace	None	—	1·90	2·85
H_2O 110° +	1·53	—	5·95	4·49	1·45	1·17
H_2O 110° −			0·45			
Total	101·16	—	99·93	98·55	98·90	100·25

a, with FeO; *b*, with La,Di; *c*, with 0·13 Al_2O_3; *d*, with 0·29 K_2O; *e*, with Di; *f*, calculated as Na; *g*, calculated as K.

THE REPORTED SOLIDIFICATION OF HELIUM.

The following letter from Sir James Dewar appeared in *The Times* of the 16th inst.:—

Sir,—As I was responsible for communicating to *The Times* a telegram from Professor Kamerlingh Onnes announcing the solidification of helium, I should like to lay before your readers an important correction resting upon the authority of a written detail of the Leiden experiments which I have recently received.

Professor Onnes has found that the helium operated upon, though purified with due care, had by some unexplained accident got mixed with a small percentage of hydrogen. The transient solidification witnessed on rapidly expanding the mixed gas from a state of high compression at a very low temperature was due to the hydrogen, of the presence of which Professor Onnes was unaware. The net result is that we are as far as ever from achieving the liquefaction or solidification of helium even as a momentary phenomenon. On the other hand, if the critical temperature of helium is no higher than 5° absolute, as Professor Onnes infers from a study of its isothermals at temperatures reached by the use of liquid hydrogen, then we may confidently predict, as stated in my Presidential Address to the British Association in 1902, that unless with costly expenditure it would be hopeless to anticipate any success in obtaining the liquid or solid in the static condition. My hopes of the Royal Institution method of attacking the problem leading to a satisfactory result were based on the assumption that the critical temperature of helium would not be lower than about 8° absolute; but if Professor Onnes is right, then it is clear that any resources I can at present command would be inadequate to settle the question.

James Dewar.

Royal Institution of Great Britain, April 14.

Royal Institution.—On Tuesday next, April 28, at 3 o'clock, Mr. Gerald Stoney begins a course of two lectures at the Royal Institution on "The Development of the Modern Turbine and its Application"; on Thursday, April 30, Mr. William Bateson commences a course of three lectures on "Mendelian Heredity" (these are the Tyndall Lectures); and on Saturday, May 2, Mr. G. F. Scott Elliot delivers the first of two lectures on "Chile and the Chilians." The Friday Evening Discourse on May 1 will be delivered by Professor Joseph Larmor, on "The Scientific Work of Lord Kelvin"; on May 8, by Mr. John Young Buchanan, on "Ice, and its Natural History"; and on May 15, by Mr. Herbert Timbrell Bulstrode, on "The Past and Future of Tuberculosis."

VOLUMETRIC METHOD FOR THE DETERMINATION OF ZINC.*

By WM. HERBERT KEEN.

SEVERAL schemes have been advanced for the estimation of zinc by titration with potassium ferrocyanide, but so far no one of them has found universal application, The methods which have found favour are either so complicated or so difficult in manipulation that a large personal error is always introduced, and it seldom happens that very close checks are obtained by different operators, even when the same procedure is followed. Nearly a year ago I became interested in the volumetric determination of this metal with the idea of substituting it for the rather tedious gravimetric method which has always been in use in the laboratory of Booth, Garrett, and Blair, of Philadelphia.

At first, and for quite a long time in fact, I was not very successful, and encountered numerous difficulties. The samples which I used in this preliminary work were spelters, the zinc content of which had been very carefully determined by difference. Finally, after a trial of all the methods which seemed reliable, with varying successes, I concluded that changes might be made to good advantage in nearly all of them, so with what experience I had already gained, I attempted to work up a scheme which would embody the good points of all of these methods, and as far as possible none of the bad ones. The method which I am about to describe, therefore, is not new, but is rather a re-modelling of the older ones. The scheme is one which is identical in certain parts for almost every condition, but there are some slight variations which are necessary for different products, and, if accuracy is desired, they should be observed. Accordingly, I will describe the method, applying it to typical cases.

Preparation of the Ferrocyanide Solution.—Dissolve crystals of chemically pure potassium ferrocyanide in water in the proportion of 22 grms. to the litre. If the solution is not clear, it should be filtered before it is diluted to the desired volume. It is a good plan to make up several litres at a time, as the solution remains constant almost indefinitely, and if many determinations are necessary, a bottle of 15, or even 20, litres of solution will not last very long.

Preparation of the Standard Zinc Solution.—This solution should be made up with the greatest care, as all subsequent work depends on its accuracy. In order to make up 2 litres, weigh very carefully, and transfer to an 800 cc. beaker 10 grms. of chemically pure zinc or an equivalent weight of the oxide (12·4465 grms.)—if the latter is used, it must be freshly ignited, cooled in a desiccator—and dissolved in 50 cc. of hydrochloric acid diluted with water. Heat until solution is complete, and then dilute to about 300 cc., and add a considerable excess of bromine water. Heat until the bromine is entirely expelled. Wash the cover-glass and the sides of the beaker, and add an excess of ammonia. Put in a warm place on the hot plate where it will remain just below the boiling-point, or boil very gently for about fifteen minutes. By this time the small amount of iron, which is nearly always present, should be completely precipitated. Filter carefully into a graduated litre flask, washing the beaker and precipitate once with water containing a little ammonia, and then several times with hot water. Replace the flask under the funnel by a small beaker (about 250 cc. capacity), and dissolve the iron precipitate in hot dilute hydrochloric acid. Re-precipitate the iron with ammonia, and filter again, adding the filtrate to the main solution. Burn the filter-paper containing the iron precipitate, and ignite. Weigh as Fe_2O_3 and calculate to Fe, deducting this weight from the original 10 grms. of zinc. Sometimes small amounts of silica and dirt are also present in the so-called chemically pure zinc, and the weight of this should also be deducted. These are small corrections, and make very little difference as a rule, but it is always well to make them, as it gives the operator more confidence in his results, and leaves no loop-hole for inaccuracy in later work. Now make the solution barely acid, using a small piece of litmus-paper as an indicator, and add 30 cc. of hydrochloric acid in excess for each litre of solution. Add also 10 grms. of ammonium chloride for each litre. Dilute to the mark with water, after cooling, and pour carefully into a *dry* 2-litre bottle. Do not wash out the flask, but after it has drained as much as it will, fill it to the mark with distilled water, and add this to the rest of the solution. Shake until thoroughly mixed, and the solution is ready for use. Its value will be 0·0050 grm. of zinc per cc. of solution—less a small correction due to the impurities deducted from the original weight.

Standardisation. — By means of standard pipettes, measure out three portions of the zinc solution of 20 cc. each, three portions of 50 cc., three of 70 cc., and three of 100 cc., into 400 cc. beakers of the wide shallow type, which will greatly lessen the amount of stirring necessary in order to obtain a homogeneous solution after each addition of the ferrocyanide. Add about 1 cc. of hydrochloric acid to each of the smaller portions. Dilute each to 150 cc., and all are ready for the titration. Except for very accurate work it is not necessary to take more than three or four portions altogether (one for each amount) to determine the average value of the ferrocyanide solution, but it has been found that a slightly different factor should be used for different amounts of zinc (*Journ. Am. Chem. Soc.*, xxix., 205), hence the necessity in accurate work for establishing these factors for amounts of solution likely to be used most frequently. Fill a clean burette with ferrocyanide, heat one of the portions of zinc chloride nearly to boiling, and titrate as follows :—Pour off about 20 cc. of the hot zinc solution into a small beaker, and set it aside. Titrate the remainder by running in ferrocyanide, a few cc. at a time, until a drop tested on a porcelain tile with a drop of 5 per cent solution of uranium acetate shows a decidedly brown colour. Now add all but about 2 cc. of the reserved portion, and having tested to be sure that the end-point is not now overstepped, add the ferrocyanide in portions of half a cc. at a time until the end-point is again passed. Finally, add the last of the reserved portion, washing it all out with distilled water, and carefully washing down the sides of the titration beaker, and finish the titration by adding two drops at a time, testing after each addition. The end-point at this time will be sharper if instead of one drop two or three drops are added to the drop of uranium acetate on the tile. The amount of zinc lost at this stage of the titration will be so small as to be insignificant. When the final distinctly brown tinge is obtained, wait a minute and observe if one or more of the preceding tests do not also develop a colour. Note the number of spots by which the end-point has been overstepped, and since each test means an addition of two drops, or 0·1 cc. of solution, make the necessary correction when reading the burette. A blank should also be made, and the final reading and all other readings corrected by this amount. The blank should be made with a solution containing 10 cc. of hydrochloric acid, neutralised with ammonia, made acid again, and after 3 cc. of acid have been added in excess, diluted to 150 cc., and heated nearly to boiling. This will usually require about 0·2 cc. to give a decided test. Run all the titrations in the same way, and calculate the values for 1 cc. of the solution for the different portions, taking the average of the three results in each case if they are close enough (it is easy to obtain checks within 0·1 cc.), thus obtaining the different factors for the varying amounts of zinc—or what is equivalent to the same thing, for varying amounts of ferrocyanide. In actual work later, the factor should be used for the amount of solution which corresponds most nearly to that required for the titration. Ordinarily, however, the one average factor for three or four different amounts of zinc will be accurate enough for all determinations.

* *Journal of the American Chemical Society*, XXX., No. 2.

The last solution which I standardised had the following factors :—

Standard zinc solution.	Grms. of zinc.	Ferrocyanide solution.	Factors.
20	0·09995	19·4	0·005152
50	0·24988	48·1	0·005195
70	0·34983	67·2	0·005206
100	0·49975	95·5	0·005233

Greater accuracy could be obtained with a slightly weaker solution, say, 15 or 18 grms. to the litre, but for general application I find a solution of the above strength the most convenient.

Determination of Zinc in a Spelter.

Method of Sampling.—There are several methods in common use, but probably the most accurate one is to break off small pieces from slabs in different parts of the pile until enough has been obtained to make a fair average—say, five pounds for each car load, if the shipment is homogeneous. The sample thus obtained should then be heated in an ordinary clay crucible until just melted, when it should be poured into a wooden box, previously rubbed with chalk—and shaken violently. A box suitable for this must be made with tight joints and no cracks, and should be supplied with a cover. This treatment should result in a finely granulated sample. Screen out the coarser pieces by passing through a 20-mesh, and reduce the bulk of the fine stuff by coning and quartering until a small working sample is obtained. This not only will be found very easy to weigh, but will in addition almost perfectly represent the whole consignment.

Analysis.—Weigh 5 grms. of the sample of spelter, place in a 600 cc. beaker, cover with a watch-glass, and dissolve in 50 cc. of hydrochloric acid (1·20) diluted with water. Heat until completely dissolved. The evolution of hydrogen, occasioned by the solution of the zinc, precipitates such metals as copper, lead, and tin; but the heating should be continued until these metals go into solution again, as they occlude small amounts of zinc. When solution is complete, neutralise with ammonia, and re-acidify with hydrochloric acid (1·20), adding 5 cc. in excess, dilute to about 300 cc., and pass a current of hydrogen sulphide gas through the warm solution for about twenty minutes. If the precipitated sulphides do not settle readily, allow the solution to stand for an hour or so at a temperature just below the boiling-point. This will not be necessary unless tin is present. Filter off the sulphides, allowing the filtrate to run into an 800 cc. beaker, and wash the filter thoroughly with hot water. Heat the filtrate to gentle boiling, and after the free hydrogen sulphide has been expelled add a large excess of bromine water, and continue the boiling until the bromine has been expelled. Now add a large excess of ammonia, and boil gently for about fifteen minutes. If the amount of iron is considerable, it will not be necessary to boil so long, as it is only in the case of very small amounts that the precipitation is likely to be incomplete, unless the boiling is continued. Filter into a graduated litre flask, washing first with dilute ammonia—both the beaker and the filter—and then with hot water. Put about 10 cc. of hydrochloric acid (1·20) in the beaker, dilute with hot water, and pour it over the precipitate on the paper, allowing it to run through into a small beaker of about 250 cc. capacity. Re-precipitate with ammonia, and filter into the main solution in the flask, washing as before. If the amount of iron is very large large, a third precipitation will be necessary, but in the ordinary spelter this is not the case. Put a small piece of litmus-paper in the flask, and add hydrochloric acid (1·20) until the solution is just acid, and then add 30 cc. in excess. Cool to room temperature, and then make up to the mark with water. After mixing the solution thoroughly by several decantations back and forth from the flask to a beaker, measure out several portions of 100 cc. each (equivalent to one-half grm. of spelter) by means of a pipette. I find it convenient to use a 400 cc. beaker for the titration. Usually only one portion is necessary, but it is well to have a second one in reserve. Dilute to 150 cc., heat nearly to boiling (about 85°), and titrate with ferrocyanide, as described in the procedure for standardisation. Calculate the percentage of zinc by multiplying the standard value of 1 cc. by the number of cc. required (less the blank), and divide by 0·5, the weight of spelter taken as a sample.

If manganese is present in the spelter—a rare occurrence—the above result will be too high. If time is an object, the quickest way to overcome this difficulty is to make a separate determination of the manganese, although it may be removed before titration in a way I shall describe later. To determine the manganese, the best and most rapid way is to use the bismuthate method as applied to steels. Dissolve 1 grm. of the spelter in a 150 cc. Erlenmeyer flask in 50 cc. of nitric acid (1 to 3), and boil off the nitrous fumes. Cool in ice-water, and add about a grm. of sodium bismuthate. If manganese is present, the pink colour of permanganic acid will develop at once. If such is the case, filter through an asbestos filter into a 300 cc. Erlenmeyer, washing with 100 cc. of ice-cold 3 per cent nitric acid. Add a measured amount of ferrous sulphate solution (12 grms. to the litre) until the solution is perfectly colourless; titrate the excess with a standard permanganate solution (1 grm. to the litre). Subtract the volume of permanganate required from the amount of the latter equivalent to the volume of ferrous sulphate used and multiply by the manganese value of the permanganate solution. The factor is about 0·00035 for a solution of this strength. This will give the percentage of manganese in the spelter. The chemical equivalent of this amount in zinc should be deducted from the percentage of zinc previously obtained.

If cadmium is present, it will also remain in solution with the zinc, and will affect the titration in a manner similar to the manganese. It is usually present in such very small amounts that it is not readily precipitated by hydrogen sulphide except from a nearly neutral solution, in which part of the zinc is also precipitated. It is therefore necessary to make a separate determination of the cadmium and correct the apparent amount of zinc, as was done in the case of manganese. Another alternative, which has given me doubtful success in the case of such small amounts, is to boil the solution for a few minutes with a piece of aluminium foil, just previous to titration. The aluminium thus introduced into the solution does not affect the result. Usually, however, unless specially asked for, cadmium is always counted as zinc.

(To be continued).

NOTICES OF BOOKS.

Fertilisers and Feeding Stuffs. By Bernard Dyer, D.Sc. Fifth Edition. London: Crosby Lockwood and Son. 1908.

This handbook is intended for the practical farmer, and in consequence the subject is treated from a more popular point of view than would be necessary or desirable if it were for the use of men who had had the advantage of some scientific training. It is extremely difficult to provide for agriculturists the information which will be immediately and practically useful to them, without wrapping it up in a covering of general preliminary explanation, which sometimes to the unskilled seems to obscure the scientific truths altogether, but the author has succeeded admirably in this little book. His evidently wide knowledge of farming practice will no doubt encourage his readers to accept his statements not as theories based upon experiments, but as facts accumulated in actual work. Of the former the farmer is suspicious, but now-a-days he is generally willing to accept the help of science if the services rendered by it on a scale comparable with his own are put definitely and clearly before him, as in

this book. The Fertilisers and Feeding Stuffs Act of 1906 is quoted in full, and notes upon it have been added by A. J. David, B.A, Ll.M.

Analytical Notes. 1907. London and Liverpool: The Laboratories of Evans Sons, Lescher, and Webb, Ltd. 1908.

THIS pamphlet contains an alphabetical list of the various drugs and chemicals which have been examined in the laboratories of Messrs. Evans Sons, Lescher, and Webb, Limited, together with notes upon the degree of purity of the different products. It gives a very good indication of what are the likely adulterations in the substances considered, and of what likelihood there is of obtaining a perfectly pure product in the market. The results of the analysis of pure specimens are compared with those of adulterated products, and in addition some methods of assay which have been perfected in the laboratories are described fully. The pamphlet will be of use to pharmaceutical chemists, who will find in it information relating to the probable adulterations and impurities in commercial samples of many important drugs.

Les Produits Industriels des Goudrons de Houilles et leurs Applications. ("The Industrial Products of Coal-Tar and their Applications"). By VLADIMIR DE VULITCH. Paris: Gauthier-Villars.

THE most important products obtained from coal-tar are considered in this book more from a commercial than scientific point of view. The reader is supposed to be acquainted with the chemical nature and properties of the substances dealt with, and only the industrial uses are discussed. These, however, are treated very fully, and practical methods of testing, which make up in speed for what they lack in accuracy, are specially emphasised. The adulteration of each product is considered, and also its valuation, while the principal conditions which a good marketable sample must fulfil are carefully explained. The applications of the various classes of products are enumerated, and chemists and manufacturers interested in coal-tar products will find that the little book contains much that will aid them in detecting the purity and estimating the value of specimens of the different products.

MISCELLANEOUS.

Tantalite in Australia.—In the Wodgina district in Western Australia a tantalite-bearing dike of pegmatite has been found near McCarthy's creek. In places the dike is almost entirely composed of the soda felspar albite, while elsewhere it is very largely quartz. Tantalite is very freely visible in the albite, in coarse pieces, often many pounds in weight. By ground-sluicing below the dike some heavy lumps have been obtained, one weighing about 500 lbs., evidently derived from the weathering-down of the pegmatite. The quantity of tantalite produced by the placer mining is 34·1 tons. The mines were worked energetically for a short time until the consumers' stocks were filled, and then the mineral could not be sold. The industrial uses of tantalite are at present very limited, and the demand for the mineral small.—*Mining and Scientific Press*, Toronto.

Vapour Densities of P_4S_3, P_4S_7, P_2S_5.—Alfred Stock.—Victor Meyer's apparatus was used to determine the vapour densities of the three sulphides of phosphorus from 600° to 1000°. All three sulphides decompose at a red heat, P_2S_5 in the neighbourhood of its boiling-point (520—530°), while P_4S_3 and P_4S_7, which boil at about 400°, have normal densities between fairly wide limits. Thus the vapour density of P_4S_3 at 700° is found to be 219 and of P_4S_7 337, while that of P_2S_5 is 185. P_4S_7 decomposes very rapidly between 750 and 800°.—*Berichte*, xli., No. 4.

MEETINGS FOR THE WEEK.

TUESDAY, 28th.—Royal Institution, 3. "The Development of the Modern Turbine and its Application," by Gerald Stoney, M.Inst.C.E., &c.
—— Royal Society of Arts, 8. "Lace as a Modern Industry," by Miss Isemonger.
WEDNESDAY, 29th.—Royal Society of Arts, 8. "Modern Roumania," by Alfred Stead.
—— Society of Dyers and Colourists, 8. "Dyeing and Colouring of Paper Pulp," by R. W. Sindall. "Germicidal Value of Petroleum Benzine," by F. J. Farrell and F. Howles.
THURSDAY, 30th.—Royal Institution, 3. (The Tyndall Lectures). "Mendelian Heredity," by William Bateson, F.R.S., &c.
—— Royal Society of Arts, 4.30. "Reminiscences of Indian Life," by the Rt. Hon. Lord Lamington, G.C.M.G., &c.
FRIDAY, May 1st.—Royal Institution, 9. "The Scientific Work of Lord Kelvin," by Prof. Joseph Larmor, Sec.R.S.
—— Royal Institution, 5. Annual Meeting.
SATURDAY, 2nd.—Royal Institution, 3. "Chile and the Chilians," by C. F. Scott Elliot, M.A., &c.

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THE CHEMICAL NEWS.

Vol. XCVII., No. 2527.

A SCHEME FOR THE SEPARATION OF THE RARE EARTHS.

By C. JAMES.

In this communication a comparatively simple scheme for the separation of mixtures of the rare earths is offered in the hope that it may prove of value to anyone who is desirous of entering this very interesting field of research. The conclusions presented are the results of several years' investigation upon the various methods proposed for fractionation, and personal trial of the applicability of many other compounds which had not previously been employed for the separation of these elements. Only those methods which proved valuable will be mentioned.

It might be as well to state in the beginning, for the benefit of those who have had little cause to study this subject, that there is no quantitative method for the separation of any of the rare earths. The true members of this family comprise those elements that are included in the cerium and yttrium groups, and are characterised by their trivalency, and the fact that they form oxalates that are insoluble in dilute acids and in cold ammonium oxalate solution.

The nearest approach to a quantitative separation is found in the case of cerium. This is due to the fact that the properties of the metals of all these earths and of their salts, with the possible exception of cerium itself, vary among themselves by very minute differences.

Bearing these observations in mind, the following scheme is presented :—The mineral is decomposed either by hydrochloric acid, sulphuric acid, bisulphate of potassium, sodium hydroxide, or hydrofluoric acid. When hydrochloric acid is used the whole is evaporated to dryness to render the silica insoluble. It is then warmed with a little concentrated hydrochloric acid, after which the mass is treated with water and filtered. The filtrate may then be precipitated either by oxalic acid or ammonium oxalate. If the liquid contains a lot of mineral acid, ammonium oxalate is to be preferred. When sulphuric acid or potassium bisulphate has been used to break up the mineral, it is necessary to stir with cold water to obtain the solution of the desired elements.

Fusion with sodium hydroxide and washing with water gives a residue of oxides. These are dissolved in hydrochloric acid. Hydrofluoric acid decomposes many minerals, such as niobates, tantalates, &c., in the cold, giving a residue of rare earth fluorides, while silicon, niobium, tantalum, &c., go into solution. The insoluble fluorides are decomposed by means of sulphuric acid.

The sulphate or chloride solutions are then precipitated either by ammonium oxalate or oxalic acid, as mentioned above.

Having obtained the earths in the form of oxalates they are treated as follows :—

Zirconium and Thorium.

Should the rare earth oxalates contain these elements, they may be separated by boiling with a solution of ammonium oxalate, when the whole of the zirconium and nearly all of the thorium pass into solution. The residue is filtered off and washed with ammonium oxalate solution. On the addition of an excess of hydrochloric acid to the filtrate, thorium oxalate alone is precipitated, while the whole of the zirconium is held in solution by the oxalic acid produced by the action of the hydrochloric acid on ammonium oxalate.

As zirconium oxalate is soluble in an excess of oxalic acid, this reagent alone may be used in the absence of thorium. In this connection it should be remembered that the oxalates of cerium and of the earths of the yttrium group are somewhat soluble in hot concentrated ammonium oxalate solution, so that varying amounts go into solution. Thorium can, however, easily be separated from the yttrium earths which remain with it by means of the double sulphate of thorium and potassium, which is insoluble in a solution of potassium sulphate, while the corresponding compounds of the yttrium group are soluble. The crude thorium oxalate is converted into sulphate, and the cold solution is stirred with solid potassium sulphate. Sulphate solutions of the earths are the best to work with for this purpose, for if other compounds are used care must be taken to keep the solution from being too concentrated, since members of the yttrium group may be precipitated also.

After the removal of the yttrium earths cerium earths are still present, and thorium may be separated from these by means of the solubility of its oxalate in ammonium oxalate, or, according to Glaser, by the solubility of thorium oxalate in ammonium acetate (*Journ. Am. Chem. Soc.*, xviii., 782); also by the method of Wyrouboff and Verneuil, in which thorium is precipitated by hydrogen peroxide (*Bull. Soc. Chim.*, [3], xix., 219). These methods are given under the separation of cerium and thorium, because under usual conditions they separate together from the rest of the rare earths.

In the next step there are three alternatives which depend upon the composition of the oxalates as approximately determined by the solubility of the double sodium or potassium sulphates in potassium or sodium sulphate solution, viz. :—(*a*) If containing 20 per cent or more of the yttrium earths and only a trace of thorium ; (*b*) if containing 20 per cent or more of the yttrium earths together with thorium ; (*c*) if containing less than 20 per cent of the yttrium earths.

(*a*) When the material consists of 20 per cent or more of the yttrium earths and practically no thorium, the oxalates are converted into sulphates by mixing with strong sulphuric acid and carefully igniting until fumes of sulphuric acid are no longer evolved. The residue is then powdered and dissolved in *ice-cold* water. The resulting sulphate solution is stirred with solid sodium sulphate, which throws down the double sulphates of sodium and the cerium earths.

Note.—Another method, which is simpler if the oxides will dissolve in acid, is to ignite the oxalates, and dissolve the oxides so obtained in hydrochloric acid or nitric acid, dilute the solution, and treat with solid sodium sulphate until the double sulphates are precipitated. However, when oxalates rich in cerium are ignited, the oxides which are formed dissolve with great difficulty in hydrochloric or nitric acid, and so in this case it is better to treat the oxalates with sulphuric acid as mentioned above. Extra care must be taken when the chlorides or nitrates in solution are stirred with solid sodium sulphate, for if the solution is too concentrated metals from the yttrium group will be precipitated also.

This precipitate contains some of the yttrium group of earths, while small amounts of samarium, gadolinium, and europium remain in solution. The precipitate is separated by filtration and washed with a solution of sodium sulphate. The insoluble double sulphates consist chiefly of cerium, lanthanum, praseodymium, neodymium, samarium, europium, and gadolinium, together with small amounts of the yttrium earths in which the terbium, dysprosium, and holmium contents are considerably increased. These double sodium sulphates constitute Fraction A. The filtrate, on the addition of an excess of oxalic acid, throws down the oxalates of terbium, dysprosium, holmium, yttrium, erbium, thulium, ytterbium, and scandium, together with some samarium, europium, and gadolinium. This precipitate forms Fraction B.

(*b*). The composition of the oxalates in this case is very similar to (*a*), the only difference being the thorium content.

The sulphate or chloride solution is treated with sodium sulphate and the insoluble double sodium cerium group sulphates, forming Fraction A, filtered off. Since sodium thorium sulphate is somewhat soluble in sodium sulphate solution, the filtrate is saturated with potassium sulphate, when the remaining thorium is precipitated as thorium potassium sulphate insoluble in potassium sulphate solution. After separating the precipitate, the filtrate is treated with an excess of oxalic acid, the insoluble oxalates being filtered off and washed. This material is added to Fraction B.

(*c*). In this, the third and last alternative, the oxalates consist almost entirely of the cerium metals, and it is best to start the work of separation from the point A.

Cerium and Thorium.

The next operation consists of separating cerium together with thorium, if the latter is present, from the other elements forming Fraction A. This is best carried out by treating the nitrate solution with an excess of zinc oxide and potassium permanganate. If the material is in the form of the insoluble double sodium sulphates it should be boiled with sodium hydroxide in excess. The resulting hydroxides are filtered off, well washed with hot water, and dissolved in nitric acid. In dealing with oxalates that contain large amounts of lanthanum, praseodymium, and neodymium, it is only necessary to ignite, when the oxides so obtained will readily dissolve in nitric acid. As a rule, when cerium is present in large amounts, since the oxide dissolves with great difficulty, the oxalates are converted into sulphates. The sulphate solution is then poured into fairly strong and boiling sodium hydroxide. The rare earth hydroxides formed under these conditions filter rapidly, and after washing with boiling water are dissolved in nitric acid. The nitrate solution obtained by any of the above methods is neutralised, stirred rapidly by a motor, and an *excess* of zinc oxide added. On the addition of potassium permanganate cerium peroxide is precipitated, and the addition is continued until the liquid, after continued stirring, remains red. This method leaves a little cerium in solution, which is separated later. The precipitate, consisting of cerium and manganese peroxides, together with thorium and a small amount of lanthanum, praseodymium, and neodymium, makes Fraction C. The filtrate is saturated with sodium sulphate, causing a precipitate of the double sulphates of sodium with lanthanum, praseodymium, neodymium, &c. This, after filtering and washing with sodium sulphate solution, constitutes Fraction D. To this last filtrate, containing small amounts of the yttrium group, an excess of oxalic acid is added. The oxalates so obtained are united with those forming B.

Thorium.

Although thorium is not now considered as a rare earth, methods for its purification do not seem to be altogether out of place. The cerium peroxide contains large amounts of manganese, which is first removed by dissolving in strong hydrochloric acid and precipitating the earths by means of solid sodium sulphate until no more insoluble double sulphates separate. The liquid is then filtered, and the precipitate washed with sodium sulphate solution. A portion of the thorium remains in the filtrate, but this can be separated either by means of oxalic acid or else by stirring with solid potassium sulphate.

The cerium sodium sulphate is boiled with an excess of sodium hydroxide, the residue filtered off, washed with boiling water, and dissolved in nitric acid. The nitrate solution is then neutralised by means of ammonia, after which peroxide of hydrogen is added (Wyrouboff and Verneuil, *Bull. Soc. Chim.*, [3], xix.-xx., No. 6; and Chemical News, lxxvii., 245), and the whole boiled for a few minutes. Some of the filtered solution should then be tested by treating with an equal volume of hydrogen peroxide and boiling, and the process repeated until no precipitate is thus obtained. The filtrate is reserved for he preparation of pure cerium, The thorium precipitate, having the composition $Th_4O_7N_2O_5$, is very impure, and may have a yellow or even an orange colour after standing for a short time.

Note.—It is highly important that the peroxide of hydrogen be free from phosphoric acid, otherwise an insoluble cerous phosphate may be thrown down with the thorium.

The crude thorium obtained above may be purified by treating the nitrate solution with an excess of warm ammonium oxalate. The soluble portion can then be converted into the oxalate, and treated again with warm ammonium oxalate.

Thorium can be separated from cerium (Glaser, *Journ. Am. Chem. Soc.*, xviii., 782) by the solvent action of ammonium acetate on thorium oxalate. This, as well as the ammonium oxalate method, can be applied to the cerium precipitate. The whole is dissolved in strong hydrochloric acid and precipitated by means of oxalic acid. Glaser says:—"Thorium is separated best by converting the oxalates into sulphates, the greater part of the free acid neutralised with ammonia, the solution boiled, and boiling ammonium oxalate added in excess. After a short time (as soon as oxalates of the cerium metals have formed, but before the liquid has cooled, a solution of ammonium acetate is added. When cold the entire cerium group is precipitated as oxalates, while thoria remains in solution. After prolonged standing, best over-night, the insoluble oxalates are removed by filtration (F); in the filtrate precipitate thoria with ammonia in excess, filter, and wash." All the thorium precipitates are accumulated at E. Another treatment or two with hydrogen peroxide in neutral nitrate solution gives a very good thorium product.

Thorium can be obtained very pure in the following manner:—Thorium hydroxide is first prepared by adding a slight excess of ammonium hydroxide to a solution of thorium nitrate and washing well the precipitate thrown down. This is then added to a solution of acetyl acetone in absolute alcohol, and the mass heated on the water-bath for a short time, after which it is filtered and allowed to crystallise. The acetyl acetonate is then placed in a very small retort and carefully distilled in a vacuum. The portion that condenses in the neck of the retort and in the receiver is dissolved in concentrated nitric acid, boiled for a short time, diluted with water, filtered, and precipitated by means of oxalic acid. Thorium oxide obtained by igniting this oxalate is absolutely snow-white, even after long ignition. A determination of the equivalent gave an atomic weight of 232·3. Thorium may also be purified by the sulphate method as follows:—Anhydrous thorium sulphate is dissolved in ice-cold water until the liquid is saturated. (According to Urbain, ammonium acetate aids the solution).

The filtered liquid is then heated to 20° C., when nearly pure thorium sulphate separates. It is then dehydrated, and the treatment repeated two or three times.

Cerium.

F is the starting-point for the preparation of pure cerium. If Wyrouboff and Verneuil's method for separating thorium has been used, the purification is easily carried out by slightly modifying the zinc oxide and potassium permanganate method. If other methods have been used it is best to convert the oxalates, &c., into nitrates. The liquid is neutralised by ammonia, and treated with hydrogen peroxide in order to remove the last of the thorium. To the solution of cerium nitrate, freed from thorium, sufficient ammonium nitrate is added to form the double salt. An excess of potassium permanganate is run in, and only enough cream of zinc hydroxide added to precipitate most of the cerium, being sure to leave some in solution, for otherwise praseodymium and neodymium will accompany the precipitate. The whole is then heated by steam, filtered, and washed with water containing a little ammonium nitrate. The precipitate is dissolved in concentrated hydrochloric acid, the solution diluted, and the cerium precipitated with oxalic acid (G). The oxalate

obtained by this method usually contains a little zinc and manganese, the latter colouring the oxide brown ; so for the final purification the oxalate is treated with a slight excess of sulphuric acid, and the whole heated until the fumes of sulphuric acid are no longer given off. The resulting sulphate is dissolved in cold water, and the filtered solution heated on the water-bath. The sulphate that separates is washed with boiling water. This material should give an oxide with only a pale yellow tint.

Note.—Praseodymium is a very common impurity found in cerium. This has been pointed out many times by different investigators, so that if very pure cerium is required one must be on his guard against this substance.

The mother-liquor is treated with oxalic acid, the oxalate which is thrown down being worked up with the next lot. The filtrate from the cerium peroxide still contains cerium, which is removed by adding an excess of zinc oxide, and more potassium permanganate should the colour be discharged. The precipitate obtained here is mixed with F. The filtrate is precipitated with an excess of oxalic acid, and the insoluble oxalates, consisting of lanthanum, praseodymium, neodymium, &c., constitute Fraction H.

Lanthanum, &c.

Fractions H and D contain lanthanum, praseodymium, neodymium, samarium, europium, and gadolinium, together with small amounts of the yttrium earths and some cerium.

These are best separated from each other by the fractional crystallisation of certain double nitrates, such as those formed by the rare earth nitrates with ammonium, magnesium, manganese, or nickel nitrate. For the separation of lanthanum and praseodymium the double ammonium nitrates are by far the best, and for separating praseodymium from neodymium the manganese salts are to be preferred. However, where one is working on the large scale it is better to start with the double magnesium nitrates, as the more soluble portions crystallise more readily than is the case with the double ammonium nitrates.

The double magnesium nitrates,—

$$2[M'''(NO_3)_3] \cdot 3[Mg(NO_3)_2] + 24H_2O$$

(Demarçay, *Comptes Rendus*, cxxx., 1019), are prepared by dissolving the rare earth oxides in a known amount of nitric acid. An equal amount of nitric acid is then neutralised by magnesium oxide, after which the two solutions are mixed and evaporated until after blowing on the surface small crystals form. Water is sprayed over the surface, and the whole allowed to crystallise for about twenty-four hours. The mother-liquor is then poured off and evaporated further, while the crystals are heated with water until dissolved, the correct amount to use being soon learned by experience. Both fractions are again allowed to crystallise for a like period, the concentration of the solutions being such that half of the solid separates on cooling. Two fractions have thus been obtained, and in subsequent fractionations the more soluble moves in one direction and the less soluble in the opposite. After the crystallisation of the second series is complete, the liquid from the most soluble portion is poured off and evaporated, while the liquid from Fraction I. is used as the solvent for the crystals forming Fraction II., adding water or evaporating as may be necessary. The least soluble portion, Fraction I., is again dissolved by heating with water. The above is repeated many times. When the fractions at either end become too small to work they should miss one crystallisation, and then be added to the next lot. After a few series of crystallisations the least soluble portion becomes very light coloured, later growing nearly colourless, and finally takes a faint green tinge. When the fractions at this end no longer show the characteristic absorption bands of neodymium, they should be placed aside and mixed together according to the amount of praseodymium contained therein ; in other words, fractions of the same colour are united.

The most soluble portion changes very rapidly. It soon takes a yellow colour, and shows a samarium spectrum, together with the bands of dysprosium, holmium, and erbium. Sometimes at this stage the liquid refuses to crystallise, or else a precipitate may form. If either of these things happens it is best to dilute with water and saturate with solid sodium sulphate to separate the yttrium earths and impurities that have accumulated and interfere with the crystallisation. The insoluble double sodium sulphates are converted back to the double magnesium nitrates in the same manner as already described, and the solution will be found to crystallise readily on evaporation. The filtrate from the double sodium sulphates is precipitated with an excess of oxalic acid, and the oxalates of the yttrium group which are thrown down are added to lot B. The neodymium bands finally become very weak in the most soluble fractions, and these are set aside for the preparation of samarium, europium, and gadolinium. After the samarium has been separated in this manner the more soluble portion of the remaining fractions rapidly turns to a beautiful amethyst, and when this occurs it is separated from the rest as neodymium. After the process has been continued a little longer it will be found that the material has been split up into four groups according to the order of their solubilities. Commencing with the least soluble, we have :—

1. Lanthanum and praseodymium.
2. Praseodymium and neodymium.
3. Neodymium.
4. Samarium, europium, and gadolinium, together with small amounts of terbium, dysprosium, &c.

Lanthanum.

Lanthanum and praseodymium are best separated from each other according to the method of Auer von Welsbach (*Monatsh. Chem.*, vi., 477), which consists of the fractional crystallisation of the double ammonium nitrates of the type $M'''(NO_3)_3.2(NH_4NO_3)+4H_2O$. These compounds are crystallised from water containing nitric acid to the extent of one-tenth the weight of the dissolved solid. To prepare the double salts the oxides are dissolved in the required amount of nitric acid, and for every three parts of acid required for the oxides two additional parts are neutralised by ammonium hydroxide. The resulting solutions are mixed, filtered, and evaporated until small crystals form on blowing over the surface of the liquid. A little water is sprayed over the surface, and the whole set aside for twenty-four hours. The process of fractionation is then carried out similarly to the double magnesium nitrates. By this method lanthanum ammonium nitrate is soon obtained perfectly colourless, and a saturated solution gives no praseodymium absorption spectrum even when observed through very thick layers. The lanthanum ammonium salt does not enclose anything like the amount of mother-liquor that the double magnesium compound does. Both cerium and praseodymium accumulate in the more soluble portion.

The colourless lanthanum salt is dissolved in water, the solution acidified and precipitated by means of oxalic acid. This oxalate is treated with a slight excess of concentrated sulphuric acid, and the whole gently ignited until all free acid has been driven off. The sulphate is powdered and dissolved in water at about 1° C. until the liquid is saturated, after which it is filtered, placed in a water-bath, and gradually raised to 32° C. The solution soon changes to a solid mass, which is placed on a Buchner funnel and washed with hot water. The few grms. that remain in solution are thrown out by means of oxalic acid. The crystallised sulphate may be rendered anhydrous and submitted once again to the sulphate method. This lanthanum gives a fine white oxide.

Praseodymium.

There are two sources for praseodymium ; firstly, from the more soluble portion obtained from the purification of lanthanum, and, secondly, from those fractions of the

double magnesium nitrates which show a strong praseodymium spectrum. These are not mixed but treated separately.

In the first case the crystallisation is carried on until no more colourless crystals separate, praseodymium accumulating in the more soluble fractions together with a little cerium.

In the second case the double magnesium salts are converted into the corresponding manganese compounds, which are finally fractionally crystallised from nitric acid of specific gravity 1·3 (Lacombe, *Bull. Soc. Chim.*, [3], xxxi., No. 10; and CHEMICAL NEWS, lxxxix., 277). In order to do this, the magnesium double salts are dissolved in water, the solution acidified, and the rare earths thrown down by oxalic acid. The oxalates obtained are washed, dried, and ignited to oxides. The oxides are then dissolved in a known amount of nitric acid. An equal amount of nitric acid is then neutralised by manganese carbonate, after which the two solutions are mixed. A precipitate of manganese peroxide is sometimes obtained at this point, but it is easily removed by adding a little oxalic acid and warming. The least soluble portion from this fractional crystallisation that no longer gives any neodymium bands in the spectroscope, is dissolved in water, acidified, and thrown down with oxalic acid. The fractions of praseodymium ammonium nitrate that are free from lanthanum are also dissolved and precipitated by oxalic acid. The praseodymium oxalate from the two sources is then united. This material may be impure owing to the presence of cerium.

Cerium can be separated in several different ways. One method consists in treating the nitrate solution with potassium permanganate and a little sodium carbonate. A separation is obtained according to Wyrouboff and Verneuil (*Bull. Soc. Chim.*, [3], xix., No. 6; and CHEMICAL NEWS, lxxvii., 254) by adding a solution of sodium acetate to a solution of the nitrates, and precipitating the cerium by hydrogen peroxide. The above methods throw down a certain amount of praseodymium also, so the precipitate should be worked up again. (Meyer and Koss, *Ber.*, xxxv., 672, recommend magnesium acetate in place of sodium acetate).

Neodymium.

Pure neodymium is obtained by continuing the crystallisation of the neodymium magnesium nitrate obtained somewhat earlier. After a few more series of crystallisations the liquid assumes a beautiful bluish lilac colour, which is seen better when some of the solution is diluted with water. On observing the spectrum, the absorption bands in the blue stand out clearly. When the solution contains samarium or praseodymium, these weaker neodymium bands are usually a little hazy. An excellent test of the purity of neodymium is found by observing the colour of the oxide, which is blue only when pure.

Samarium and Europium.

Samarium, europium, and gadolinium are contained in the mother-liquors which were obtained during the fractionation of the double magnesium nitrates. The solutions are evaporated, and the residue fractionally crystallised from nitric acid of 1·3 specific gravity (Demarçay). The addition of the isomorphous bismuth magnesium nitrate aids enormously in the separation of these elements, as Urbain and Lacomb have shown (*Comptes Rendus*, cxxxvii., 792; cxxxviii., 84). Its solubility places it between samarium and europium, and it also assists in the crystallisation of the syrupy mother-liquors, inasmuch as it carries down with it the more crystallisable portions. Samarium is obtained from the least soluble fractions. Europium is separated from the excess of bismuth magnesium nitrate which is found between the samarium and gadolinium fractions. The bismuth is thrown down by hydrogen sulphide, and the mother-liquor precipitated by means of oxalic acid.

Gadolinium.

The fractions between europium and dysprosium, &c., consist mainly of gadolinium magnesium nitrate. These solutions are acidified, and the gadolinium thrown down as oxalate. This is then washed and ignited to oxide. The resulting oxide is converted into the double nickel nitrate of the type $2Gd(NO_3)_3.3Ni(NO_3)_2+24H_2O$ (Urbain, *Comptes Rendus*, cxl., No. 9), which is then fractionally crystallised from nitric acid of density 1·3. Terbium is left in the most soluble portion.

NOTE.—The writer is applying the bromate method to a complicated mixture of samarium, gadolinium, terbium, dysprosium, and holmium, and is obtaining interesting results.

Fraction B contains oxalates of terbium, dysprosium, holmium, yttrium, erbium, thulium, ytterbium, and scandium. This material is converted into the anhydrous sulphate, the latter dissolved in cold water, and poured over an excess of barium bromate (James, *Journ. Am. Chem. Soc.*, xxx., 182; and CHEMICAL NEWS, xcvii., 61). The whole is well stirred and placed on the water-bath. After the double decomposition is complete, *i.e.*, when the clear liquid gives no precipitate with barium bromate solution after diluting and boiling, the mass is filtered and evaporated until a drop removed on the end of a glass rod nearly solidifies when stirred on a watch-glass. A little water is then sprayed on the surface, and the whole submitted to fractional crystallisation. The absorption spectrum soon shows that a rapid change is taking place. Small amounts of samarium and gadolinium are rapidly separated in the least soluble portion, while the next fractions contain terbium, and give oxides of a deep red brown colour. Dysprosium and holmium are more soluble than terbium. Yttrium places itself between holmium and erbium.

NOTE.—The writer, in a previous paper describing the serial order of the bromates, made an error in the position of yttrium (CHEMICAL NEWS, xcvii., p. 61). This element, as stated above, ranges itself in the fractions between holmium and erbium. The cause of the error was due to the fact that the material on which the serial order was worked out contained only a little yttrium and a fair amount of gadolinium. At the time gadolinium was not suspected, and the colourless bromate crystals were supposed to be due to yttria.

The most soluble portion contain erbium, thulium, and ytterbium.

Terbium, Dysprosium, and Holmium.

These elements are extremely difficult to separate. Operations with the bromates are still in progress. Terbium separates in the least soluble, together with samarium and gadolinium. The separation of dysprosium from holmium is extremly slow, and so much so that the bromate method is of no value for this work. Urbain recommends the fractionation of the double nickel nitrates from nitric acid of density 1·3 to separate samarium and gadolinium from terbium, dysprosium, and holmium. The more soluble portion, consisting of terbium, &c., with some gadolinium, is converted into the simple nitrate, and fractionally crystallised from concentrated nitric acid in the presence of bismuth nitrate. Terbium collects with the bismuth nitrate in the fractions between gadolinium and dysprosium. Fractional crystallisation of the ethyl sulphates gives dysprosium. Small amounts only of dysprosium and terbium have been separated. The preparation of pure holmia has not yet been accomplished.

Yttrium.

Yttrium is obtained from the bromate fractions between holmium and erbium. Some fractions show holmium bands in addition to erbium. It is most easily prepared from the fractions that are free from holmium. The earths are precipitated from dilute boiling solutions of the bromates by the addition of boiling potassium hydroxide solution. The hydroxides are filtered off, washed, and

converted into the nitrates. Yttrium is then separated by the method of Muthmann and Rolig (*Ber.*, xxxi., 1718) as follows :—The concentrated neutral nitrate solution is boiled, and a thick cream of magnesium oxide added until the liquid no longer gives the absorption bands of erbium. The fractions that contain holmium in addition to erbium can be put through the same process. Yttrium oxide, obtained by the bromate and magnesium oxide methods, is snow-white, and absolutely free from terbium, &c.

Erbium, Thulium, Ytterbium, and Scandium.

These elements are separated from each other by the continued fractionation of the most soluble portion of the bromates. The erbium solutions become of a beautiful rose tint. Thulium collects between erbium and ytterbium. The mother-liquor contains ytterbium with a very little scandium. The neutral solution is saturated with potassium sulphate when scandium potassium sulphate separates, as it is insoluble in potassium sulphate solution. The filtrate, on the addition of oxalic acid, gives a precipitate of ytterbium oxalate.

The fractionation of the least basic earths is still being carried on with the object of preparing pure thulium for a determination of the atomic weight, and also to confirm Urbain's lutecium.

In conclusion, I again thank the Welsbach Company for large amounts of material received through the courtesy of Dr. H. S. Miner. I also tender my thanks to the Christiania Minekompani, of Christiania, Norway, for many mineral specimens for examination.

New Hampshire College, Durham, N.H.
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THE ATOMIC WEIGHT OF TELLURIUM.

By H. BRERETON BAKER, M.A., D.Sc., F.R.S.

In December, 1907, a paper on this subject (*Journ. Chem. Soc.*, xci., 1849) was published by Mr. A. H. Bennett and myself, showing that the atomic weight was unchanged when the element was subjected to eight different methods of purification, each of which might have been expected to separate any foreign element present. The atomic weight of the highly purified element was determined by two independent methods, one of which gave the number 127·60 and the other 127·61. Simultaneously there appeared a paper by Prof. W. Marckwald (*Berichte*, 1907, xl., 4730) describing experiments on the fractional crystallisation of telluric acid. This was one of the methods tried by us, and in the hands of Prof. Marckwald, as in ours, it led to no splitting up of the element. An important difference in our results and his, however, is seen in the number found for the atomic weight. From the determination of the loss in weight of crystallised telluric acid ($H_2TeO_4 \cdot 2H_2O$), Prof. Marckwald comes to the conclusion that the atomic weight of tellurium is 126·85, compared with iodine 126·97. This result, if confirmed, would be of the greatest possible interest as removing one of what have been called "the two blots on the periodic system." The determinations, however, were made with a substance containing water of crystallisation. It has been pointed out by chemists distinguished in this most delicate branch of enquiry (Mallet, "Stas Memorial Lecture," *Journ. Chem. Soc.*, 1902, 204; Richards, *Zeit. Phys. Chem.*, xlvi.) that there is always great danger in using such substances for atomic weight determinations. Mr. Bennett and I, in the paper referred to above, mentioned that twenty-six determinations of the atomic weight of tellurium were done by us by finding the ratio of $H_2TeO_4 \cdot 2H_2O : TeO_2$. The acid had been very carefully purified, and crystallised as quickly as possible in order to obtain the crystals as small as possible. The acid was placed in a porcelain boat; this was placed in a thin Jena glass tube which served to prevent loss by the small volatilisation of the dioxide, both boat and tube being weighed together against a similar counterpoise. During the heating a slow current of dried air was drawn through the tube. The operation was carried on at as low a temperature as possible, and was complete usually in twelve hours. The fine crystals of the acid were dried in different ways : in air at the ordinary temperature, *in vacuo*, and in air over calcium chloride, over sulphuric acid, and over phosphorus pentoxide. The results obtained varied between 126·8 and 128·2 (O = 16). Treated in the same way the same acid gave the same result, but varying the treatment by more complete drying or by powdering gave widely varying numbers. Some of the fine crystals dried over sulphuric acid, which gave an atomic weight of 127·2, were powdered to an impalpable dust in an agate mortar. This then gave after standing in a desiccator over sulphuric acid for twenty-four hours an atomic weight of 127·6. It was thought that some of the water might have been driven off by the heat produced in grinding. Some of the original crystals were therefore ground under a saturated solution of the same acid, drained on a platinum plate pierced with extremely small holes, powdered again when moist, and again dried. The atomic weight obtained from them was 126·9. It seemed to us necessary to abandon the method not only on account of the doubt attaching to the constancy of the water of crystallisation, but also on account of the possibility of water being included in the crystal. In large crystals of the acid there is often seen a phenomenon which points to this inclusion. When first prepared the crystals are wonderfully bright and clear. On standing for a few hours in air, moist or dry, there frequently appears an opacity in the interior of the crystal. This probably indicates the inclusion of a saturated solution inside the crystal.

Again, telluric acid crystals show very marked crackling on heating, and this, as in the analogous cases of potassium chlorate and sodium chloride, is probably due to included water. What holds for the large crystals probably holds for the very small ones, though, of course, in a minor degree. Lastly, experiments were done by Mr. Bennett and myself which render it almost certain that the water in crystallised telluric acid is not constant; in these the residues of tellurium dioxide in two determinations, performed by heating the crystallised acid, which gave atomic weights of 126·8 and 128·0, were used for further atomic weight determinations by the sulphur method. The numbers obtained were practically identical, 127·64 and 127·62. It is to be hoped that Prof. Marckwald will apply some other method of atomic weight determination to his material, with the view of finding out if the above objections apply to the determinations which he has made.

With regard to the experiments on silver telluride ores described by Mr. Bettel (Chemical News, xcvii., 169), I fear that the interesting phenomenon which he discovered cannot be ascribed to the presence of a missing element. On reading his paper it occurred to me that the difference which he noticed in the cupellation of the silver buttons might be due to the way in which the tellurium was combined with the silver. I happened to have a specimen of silver tellurate which had been prepared from telluric acid which had been purified in the most careful way by (1) fractionally crystallising telluric acid, (2) converting into the dioxide, (3) reduction to the element, (4) conversion into the hydride, and (5) oxidation to the acid. The silver was prepared for atomic weight work by Stas's method. This silver tellurate was reduced to telluride by heating in very pure hydrogen. The telluride was cupelled with lead in the ordinary way, and immediately the "brightening" of the bead took place, the bead spread out, wetting the surface of the cupel to a nearly complete circle of 2 cm. in diameter. The description which Mr. Bettel gives of his experiment coincides in every respect with the above, and there is little doubt that the phenomena were due to the same cause. His experiment of adding tellurium to silver and cupelling was then repeated, the

tellurium being of the highest degree of purity. Again, his result, that the spreading only took place to the extent of 2 mm. round the bead, was confirmed. As it was possible that in the latter case most of the tellurium was volatilised before it entered into combination with the silver, some highly purified tellurium was heated on pure silver foil to low redness in a slow current of hydrogen. The resulting telluride was then cupelled with lead, and the spreading again took place. Lastly, some tellurium dioxide of the highest degree of purity was mixed with molecular silver and sugar charcoal and heated to low redness in a cupel. The bead of telluride was then cupelled with lead, and again the spreading took place. Some of the film was detached from the cupel, and was found to contain a considerable proportion of tellurium, and on heating the rest to the highest temperature of the furnace, fumes of tellurium dioxide were seen in the muffle, and at the end of an hour a bead of silver was obtained which did not spread at all, and which on testing was found to contain only traces of tellurium.

Hence the experiment of Mr. Bettel, interesting though it is in itself, can be repeated with tellurium which has been carefully purified, and the explanation of it seems to be simply that silver telluride has a lower surface tension than pure silver. I am afraid I know little of silver telluride ores, but if they are similar to gold telluride ores there is a possible explanation of the fact that Mr. Bettel's result was found in only one ore among the many tried. Ores of gold containing tellurium contain it in the deeper levels as telluride of gold, while in the ores obtained nearer the surface the gold is free and the tellurium is partly free and partly as the dioxide. An ore from the deeper levels might therefore show the phenomenon of spreading on cupellation, while that from nearer the surface might contain so little of the tellurium in combination with the silver as to fail in giving this result.

Christ Church, Oxford.

THE CENTENARY OF DAVY'S DISCOVERY OF THE METALS OF THE ALKALIS.*

By Prof. T. E. THORPE, C.B., Ph.D., LL.D., D.Sc., F.R.S.

(Concluded from p. 196).

SIR JAMES DEWAR has been so good as to have prepared for me a photographic reproduction of a water-colour drawing of the laboratory of the Royal Institution as it existed in Davy's time, showing the actual spot where the isolation of the metals of the alkalis was first effected.

The publication of Davy's discovery created an extraordinary sensation throughout the civilised world, a sensation not less profound, and certainly more general from its very nature, than that which attended his lecture of the previous year. But at the very moment of his triumph, it seemed that the noise of the universal acclaim with which it was received was not to reach him. I have already made reference to the condition of mental excitement under which the discovery was made and prosecuted. Almost immediately after the delivery of his lecture he collapsed, struck down by an illness which nearly proved fatal, and for weeks his life hung on a thread. He had been in a low feverish condition for some time previously, and a great dread had fallen upon him that he should die before he had completed his discoveries. It was in this condition of body and mind that he had applied himself to the task of putting together an account of his results. Four days after this was given to the world he took to his bed, and he remained there for nine weeks. Such a blow following hard on the heels of such a triumph aroused the liveliest sympathy. The doors of the Royal Institution were beset by anxious inquirers, and written reports of his condition at various periods of the day had to be posted in the hall. The strength of the feeling may be gleaned, too, from the sentences with which the Rev. Dr. Dibdin, who had been hurriedly engaged to take his place in the theatre, began the lecture introductory to the Session of 1808.

"The Managers of this institution have requested me to impart to you that intelligence, which no one who is alive to the best feelings of human nature can hear without the mixed emotion of sorrow and delight.

"Mr. Davy, whose frequent and powerful Addresses from this place, supported by his ingenious experiments, have been so long and so well known to you, has, for the last five weeks, been struggling between life and death. The effects of these experiments recently made in illustration of his late splendid discovery, added to consequent bodily weakness, brought on a fever so violent as to threaten the extinction of life. Over him it might emphatically be said in the language of our immortal Milton, that—

'. . . . Death his dart
Shook, but delayed to strike.'

"If it had pleased Providence to deprive the world of all further benefit from his original talents and intense application, there has certainly been sufficient already effected by him to entitle him to be classed among the brightest scientific luminaries of his country."

After having, "at the particular request of the Managers," given an outline of Davy's investigations, Dr. Dibdin proceeded to say:—

"These may justly be placed among the most brilliant and valuable discoveries which have ever been made in chemistry, for a great chasm in the chemical system has been filled up; a blaze of light has been diffused over that part which before was utterly dark; and new views have been opened, so numerous and interesting, that the more any man who is versed in chemistry reflects on them, the more he finds to admire and heighten his expectation of future important results.

"Mr. Davy's name, in consequence of these discoveries, will be always recorded in the annals of science amongst those of the most illustrious philosophers of his time. His country, with reason, will be proud of him, and it is no small honour to the Royal Institution that these great discoveries have been made within its walls—in that laboratory, and by those instruments which, from the zeal of promoting useful knowledge, have, with so much propriety, been placed at the disposal and for the use of its most excellent professor of chemistry."

And now, in the few minutes that remain to me, let me indicate what has been the outcome of this great and fundamental discovery. How far has the expectation of future important results been realised? Have sodium and potassium at all justified the hope that they would facilitate the means of procuring the comforts and conveniences of life?

I have not the time, even if I had the intention, to attempt to follow the many changes in the metallurgy of the metals of the alkalis of the past century. Let me at once proceed to show how the matter stands at the end of a hundred years.

The general properties and chemical activities of potassium and sodium are so very similar that as a matter of commercial production that metal which can be most economically obtained is necessarily the one most largely manufactured, and of the two that metal is sodium. To-day, sodium is made by thousands of tons, and by a process which in principle is identical with that by which it was first made by Davy, *i.e.*, by the electrolysis of fused caustic soda. It is very significant that after a series of revolutions in its manufacture, sodium, having been produced from time to time on a manufacturing scale by a variety of metallurgical methods involving purely thermal processes of reduction and distillation, entirely dissociated from electricity, we should have now got back to the very principle of the process which first brought the metal to

* A Discourse delivered before the Royal Institution, January 17, 1908.

light. And that this has been industrially possible is entirely owing to another of Davy's discoveries—possibly indeed the greatest of them all—Michael Faraday. As we all gratefully acknowledge, it is to the genius and labours of Faraday—Davy's successor in this place—that the astonishing development of the application of electrical energy which characterises this age has taken its rise.

The modern method of production of sodium is based, therefore, as regards principles upon the conjoint labours of Davy and Faraday.

These principles took their present form of application at the hands of a remarkably talented American—Mr. Hamilton Y. Castner—whose too early death, in the full vigour of his intellectual powers, was an incalculable loss to metallurgical chemistry. It is by Castner's process that all the sodium of to-day is manufactured.

In the Castner process melted caustic soda produced by the electrolysis of a solution of common salt by a method also devised by Castner, is brought into an iron vessel shaped like a large cauldron, mounted in brickwork, and provided with an extension adapted to receive the negative electrode. Suspended directly above the cathode is an iron vessel attached to a lid; to its lower edge is secured iron-wire gauze, which, when the receptacle is in position, completely surrounds the cathode. The positive electrode is connected with the lid of the vessel, which is provided with openings for the escape of the gases resulting from the electrolysis, and is suitably insulated.

As the electrolysis proceeds the alkali metal, being much lighter than the molten caustic, rises from the negative electrode and passes into the receiver, the gases escaping around the edges of the cover. The molten metal collects on the surface of the caustic, and is removed by means of a large perforated spoon, the perforations enabling the melted caustic to flow out, while the metal remains in the spoon. As the several vessels are thus skimmed in succession the fused sodium is collected into an iron vessel, whence it is poured into moulds in which it congeals, forming blocks of the size and shape of an ordinary building brick. These, after being trimmed to remove adherent oxide, are immersed in paraffin oil, and are then packed into large iron drums holding about 6 or 7 cwt., capable of being closed air-tight, and protected in transit by an outer casing of wood.

The due regulation of the volume and intensity of the current is a matter of the greatest importance in order to obtain the most economical yield of the metal. No very high temperature is needed; indeed, the temperature of the fused caustic soda should not be much higher than that of its melting-point. By suitably regulating the current, the soda, in fact, may be maintained at the proper temperature and in the proper degree of fluidity without extraneous heat. Fresh melted caustic soda is added to the vessel from time to time to replace the metal removed, and in this manner the process is made continuous.

The Castner process is now worked in England at Wallsend-on-Tyne, and at Weston Point, in Cheshire; at Rheinfelden, in Germany; at Clavaux, in France; also in Switzerland, and at Niagara, in America. The present yearly output amounts to about 5000 tons, but the plant already laid down is capable of producing at least twice this quantity.

The greater quantity of the sodium made in England is sent to Glasgow, where it is converted into sodium cyanide by the Cassel Cyanide Company for use in the extraction of gold. As gold is, I suppose, generally considered the principal material factor in procuring the comforts and conveniences of life, Davy's great discovery may be thus said to have secured the primary object which the projectors of the Royal Institution had in view. Other important uses of sodium are in the manufacture of peroxide for bleaching purposes, of artificial indigo, and of a number of other synthetic dye stuffs and of drugs like antipyrin.

It need hardly be said that this extraordinary development of the manufacture has not been without its influence on the price of sodium. A quarter of a century ago it was a comparatively rare metal, and a stick of it was regarded as a chemical curiosity, to be handled with circumspection and care. Even as late as 1890 its selling price was as high as 8s. per lb. To-day it is 8d. Sodium now takes rank, therefore, with zinc, tin, copper, or aluminium as a common, ordinary metal of commerce.

I am indebted to the directors of the Castner-Kellner Company, and in particular to my friends Sir Henry Roscoe and Mr. Beilby, for affording me the opportunity, in connection with this lecture, of actually witnessing the modern process of manufacturing sodium as it is carried out at Wallsend; and I am further indebted to Mr. Beilby for the loan of the lantern slides and specimens with which I have sought to illustrate that process.

And in concluding may I be permitted to recall here the feelings to which that visit to Wallsend gave rise. There, grouped together on the very spot where ended the old wall—the visible symbol of the power and might of a civilisation long since passed away—were some of the characteristic signs of another civilisation ampler and more beneficent. Before me, stretching down to the river, was the factory where a score of workers, clad in helmets and gauntlets and swathed like so many Knights Templar, travel-stained and war-worn, their visages lit up by the yellow soda flames, and their ears half-deafened with the sound of exploding hydrogen—a veritable inferno—were repeating on a Gargantuan scale the little experiment first made a century ago in the cellars of this building; turning out, day and night, hundredweights of the plastic metal in place of the little pin-heads which then burst upon the astonished and delighted gaze of Davy. Behind me was the magnificent power-house—one of the most magnificent of its kind in the world—furnishing not only the electrical energy which transformed the soda into sodium, but diffusing this energy for a multitude of other purposes over an entire district—a noble temple to the genius and prescience of Faraday. Surely one might here say, if you desire to see the monuments of these men, look around! And to my right, and close at hand, was the huge building slip just vacated by the *Mauretania*, herself a symbol of the supremacy of an empire, far mightier, more world-wide, and more potent for good than that which massed its legions behind the old wall.

Iron and Steel Institute.—*Annual Meeting*, 1908.—The Annual Meeting of the Institute will be held at the Institution of Civil Engineers, Great George Street, Westminster, on Thursday and Friday, May 14 and 15, 1908, commencing each day at 10.30 a.m. Thursday, May 14: General Meeting of Members. The Bessemer Gold Medal for 1908 will be presented to Mr. Benjamin Talbot (Middlesbrough). At 7 p.m., Annual Dinner of the Institute in the Grand Hall of the Hotel Cecil. Friday, May 15: General Meeting of Members. The awards of the Andrew Carnegie Gold Medal and Research Scholarships for 1908 will be announced. *Autumn Meeting.*—The Council has accepted a cordial invitation to hold the Autumn Meeting of the Institute in Middlesbrough on September 29, and following days. *Visit to Canada.*—The Canadian Mining Institute is arranging for an excursion in September, 1908, to the mineral areas of Eastern Canada, including the silver-cobalt ore region, the nickel mines, and the iron ore mines of Ontario, the asbestos and chromite regions of the Province of Quebec, and possibly the coal and iron areas of Nova Scotia. It is expected that the excursion will extend over a period of three weeks. The Canadian Mining Institute has extended to the members of the Iron and Steel Institute a cordial invitation to take part in this excursion, and any members wishing to avail themselves of this kind invitation are requested to communicate with Mr. H. Mortimer Lamb, Secretary of the Canadian Mining Institute, 413, Dorchester Street West, Montreal, Quebec.

EXPLOSIVE COMBUSTION, WITH SPECIAL REFERENCE TO THAT OF HYDROCARBONS.*

By Professor WILLIAM ARTHUR BONE, D.Sc., Ph.D., F.R.S.

(Concluded from p. 198).

Having thus, I hope, explained the main issues involved in the controversy, I shall now proceed to perform a series of experiments on the explosive combustion of acetylene, ethylene, and ethane, some of which are crucial as regards the rival theories under discussion.

Experiment II.

I have here three cylindrical bulbs of stout borosilicate glass (capacity = about 60 cc.), fitted with firing wires, hermetically sealed, and containing respectively equimolecular mixtures of each of the three hydrocarbons with oxygen, that is to say, mixtures corresponding to $C_2H_2 + O_2$, $C_2H_4 + O_2$, and $C_2H_6 + O_2$, respectively.

Now, according to the theory of the preferential combustion of carbon, these mixtures should, on explosion, yield nothing but carbonic oxide and hydrogen, without any separation of carbon, or formation of steam, as follows :—

	p_2/p_1.
(*a*) $C_2H_2 + O_2 = 2CO + H_2$	1·5
(*b*) $C_2H_4 + O_2 = 2CO + 2H_2$	2·0
(*c*) $C_2H_6 + O_2 = 2CO + 3H_2$	2·5

(The symbols p_1 and p_2 used in this and subsequent tables denote the initial and final pressures of the *cold* original mixture and gaseous products, dry, at constant volume and at the same temperature).

On firing the mixtures, it is at once evident that something very like this does happen in the cases of (*a*) and (*b*). There is absolutely no deposition of carbon, and no appreciable condensation of steam in the cold products. Far otherwise is it, however, in the case of the bulb containing the mixture $C_2H_6 + O_2$. A lurid flame fills the vessel, accompanied by a black cloud of carbon particles, and a close inspection of the cold bulb will reveal a considerable condensation of water. The pressure ratio p_2/p_1 is approximately 1·5, and an analysis of the gaseous products would prove the presence of about 10 per cent of methane. The bulb will now be opened, rinsed out with water, and the formation of aldehydic products demonstrated by means of Schiff's reagent. It is clear that these results are wholly inconsistent with the theory of the preferential burning of carbon.

As it is obviously impracticable for me to complete the experiment by analysing the gaseous products before you, I will draw your attention to the following tabulated results of three similar experiments carried out some time ago. (Table I.).

Did time permit, I could easily demonstrate to you by other similar experiments, that the *outward* difference here revealed between the burning of ethylene and that of ethane extends to all the other gaseous olefines and paraffins ; that is to say, whereas mixtures of olefines and oxygen corresponding to $C_nH_{2n} + n/2\ O_2$ on explosion yield mainly carbonic oxide and hydrogen, without separation of carbon, mixtures of paraffin and oxygen corresponding to $C_nH_{2n+2} + n/2\ O_2$ yield carbon, oxides of carbon, methane, hydrogen, and steam, all in considerable quantities. Are we then to conclude that there is some peculiarity about the constitution or combustion of an olefine which induces a preferential burning of its carbon, whilst the corresponding paraffin is burnt in an entirely different way ? The following experiment will show that such a view cannot for a moment be entertained.

Experiment III.

I will now fire a bulb containing a mixture of 60 per cent of ethylene and 40 per cent of oxygen (*i.e.*, $3C_2H_4 + 2O_2$). As might be expected, the flame is accompanied by a large deposition of carbon, but what is of greater importance still is the fact that a considerable amount of water is also formed. The full significance of this experiment may be gathered from the following data.

Original mixture { $C_2H_4 = 59{\cdot}65$ per cent. $p_1 = 562$ mm. $p_2/p_1 = 1{\cdot}45$; $O_2 = 40{\cdot}35$,, $p_2 = 816$,,

Gaseous products { $CO_2 = 2{\cdot}5$, $CO = 37{\cdot}2$, $C_2H_2 + C_2H_4 = 6{\cdot}4$, $CH_4 = 6{\cdot}5$, $H_2 = 47{\cdot}4$ per cent.

	C	H	O
Units in original mixture ..	670	670	227
Units in gaseous products..	482	572	172
Difference	188	98	55

I think it will be now admitted that such an experiment as this completely destroys the foundations of the theory of the preferential burning of carbon. As I have already stated, the original experimental basis of the theory was the behaviour of an equimolecular mixture of ethylene and oxygen, yet here is proof that on closer examination the behaviour of ethylene is inconsistent with the theory. I would therefore say to those who may be inclined to cavil at my views as to the mechanism of combustion, that whatever may be the final issue of the controversy, this fact, amongst others, must be explained, namely, that whereas a mixture of an olefine and oxygen corresponding to $C_nH_{2n} + n/2\ O_2$, yields mainly carbonic oxide and hydrogen on explosion, in harmony with the equation $C_nH_{2n} + n/2O_2 = nCO + nH_2$, a diminution of the oxygen below this limit at once gives rise to steam formation.

Experiment IV.

The next experiment is designed to illustrate the infinitely greater affinity of acetylene and ethylene as compared with that of hydrogen for oxygen at the high temperatures of flames. I have here two bulbs containing mixtures of each of these hydrocarbons with hydrogen and oxygen corresponding to $C_2H_2 + 2H_2 + O_2$ and $C_2H_4 + H_2 + O_2$ respectively, and I will ask you to contrast the behaviour of these with that of the equimolecular mixture of ethane and oxygen, $C_2H_6 + O_2$, which was exploded a few minutes ago. It should be noted that whilst all three mixtures contain the same relative proportions of carbon, hydrogen, and oxygen, they differ in respect of the proportions between the combined carbon and hydrogen. Asking you to bear in mind how the equimolecular mixture of ethane and oxygen on explosion gave rise to a black cloud of carbon and a considerable formation of water, I will now fire the other two mixtures. You will observe that in neither case has there been any deposition of carbon, and an inspection of the cold bulbs will show that little or no steam formation has occurred. In fact, the hydrocarbon has been burnt to carbonic oxide and hydrogen, leaving the hydrogen absolutely untouched by the oxygen, as the following detailed results show (Table II.).

These experiments have an important bearing on the chemistry of flames. Hydrogen is usually considered as one of the most combustible of gases, but here we see it pushed to one side by the all-powerful hydrocarbon, as though it were so much inert nitrogen. This at once raises another question which has lately been occupying my attention. Ever since Davy's experiments on flame, the combustibility of hydrogen has been considered to be superior to that of methane ; this, however, cannot be true in regard to slow combustion, since it can be easily proved that between 300° and 400° C. methane is oxidised at a far faster rate than hydrogen. Nevertheless, I have recently observed facts which incline me to think that possibly it may be true in regard to flames. If further investigation confirms this opinion, it will be necessary to enquire into the cause of the peculiar relative inertness and stability of methane as compared with other gaseous

* Discourse delivered before the Royal Institution, February 28, 1908.

TABLE I.—*Results of Experiments on Inflammation in Sealed Glass Bulbs.*

Original mixture	$C_2H_2+O_2$.	$C_2H_4+O_2$.	$C_2H_6+O_2$.
p_1	352 mm.	545 mm.	746 mm.
p_2	508 ,,	1053 ,,	1148 ,,
p_2/p_1	1·44	1·93	1·54
Composition of gaseous products (per cent)—			
CO_2	0·75	0·30	4·20
CO	67·10	50·00	33·55
$C_2H_2+C_2H_4$	Nil	Nil	2·75
CH_4	1·55	1·70	10·85
H_2	30·60	48·00	48·60

	C.	H.	O.	C.	H.	O.	C.	H.	O.
Units in original mixture	352	176	176	545	545	272	746	1119	376
Units in gaseous products	352	171	175	547	541	267	621	854	241
Difference	Practically nil			Practically nil			125	265	135

TABLE II.—*Experiments on Inflammation in Sealed Glass Bulbs.*

Original mixture	$C_2H_4+H_2+O_2$.	$C_2H_2+2H_2+O_2$.
p_1	503 mm.	534 mm.
p_2	750 ,,	653 ,,
p_2/p_1	1·49	1·22
Composition of gaseous products (per cent)—		
CO_2	0·35	0·2
CO	39·60	39·8
$C_2H_2+C_2H_4$	1·25	Nil
CH_4	3·65	0·2
H_2	55·15	59·8

	C.	H.	O.	C.	H.	O.
Original mixture	341	505	168	267	400	133
Gaseous products	346	478	151	262	394	131
Difference	—	27	17	Negligible		

TABLE III.—*Inflammation of an Equimolecular Mixture of Ethane and Oxygen.*

	A. In long tube.		B. In large globe.	
p_1	701 mm.		685 mm.	
p_2	1018 ,,		1187 ,,	
p_2/p_1	1·45		1·73	
Composition of gaseous products (per cent)—				
CO_2	4·20		3·40	
CO	34·80		36·10	
C_2H_2	5·00	7·65	0·15	
C_2H_4	2·65			
CH_4	8·85		7·25	
H_2	44·50		53·05	

	C.	H.	O.	C.	H.	O.
Original mixture	694	1041	354	678	1017	346
Gaseous products	643	738	220	558	805	255
Difference	51	303	134	120	212	91
Difference (per cent)	7·6	29	37·8	18	20	27·5

TABLE IV.—*Results of Explosion of an Equimolecular Mixture of Ethane and Oxygen under High Pressures.*

	A. Detonation in lead coil.	B. Explosion in steel bomb.
p_1	1180 mm.	25·2 atmos.
p_2	2240 ,,	51·7 ,,
p_2/p_1	1·90	2·05
Composition of gaseous products (per cent)—		
CO_2	1·80	2·6
CO	39·10	37·2
C_2H_2	0·90	Nil
C_2H_4	0·50 (1·40)	
CH_4	7·70	7·0
H_2	50·00	52·2

	A. C.	A. H.	A. O.	B. C.	B. H.	B. O.
Original mixture	1186	1779	587 mm.	25·35	38·0	12·55 atmos.
Gaseous products	1151	1507	488 ,,	24·50	34·6	11·05 ,,
Difference	35	272	99 ,,	0·85	3·4	1·5
Difference (per cent)	3	15	17	3·4	9	12·0

hydrocarbons when subjected to the action of oxygen at high temperatures.

It does not, I think, impose too great a strain on the imagination to picture the probable mechanism of combustion in hydrocarbon flames, and for this purpose ethylene and ethane may be taken as typical examples. It may be assumed that, with the possible exception of methane, the affinity of a hydrocarbon for oxygen is so great at high temperatures that the initial stage of its combustion takes precedence of all other chemical phenomena in flames. This is probably true of the propagation of flame through explosive mixtures of hydrocarbons and oxygen. In the special case of a stream of a hydrocarbon burning in air, partial decomposition may occur in the innermost regions of the flame, where the supply of oxygen is very limited, before combustion begins. But, in general, whenever the hydrocarbon and oxygen are brought together at high temperatures, their mutual affinities will prove superior to any disruptive forces which would otherwise break down the hydrocarbon. It is probably not so much the original hydrocarbon as its hydroxylated molecule which decomposes in flames; the

sudden increase in the internal energy of the hydrocarbon molecule, consequent upon its initial association with oxygen, would render the resulting hydroxylated molecule extremely unstable, and, in default of its immediate further oxidation, it would speedily decompose. The explosive combustion of ethylene may, therefore, be represented by the following scheme:—

$$H_2\overset{0}{C}{:}CH_2 \rightarrow HO.\overset{1}{C}H{:}CH_2 \rightarrow HO.\overset{2}{C}H{:}CH.OH$$

$$\left\{\begin{matrix}C_2H_2+H_2O\\ 2C+H_2+H_2O\end{matrix}\right\} \qquad 2CH_2O=2CO+2H_2$$

In a sufficient supply of oxygen the transition from the original hydrocarbon to the *dihydroxy* state is probably so rapid that no breaking down of the ethylenic structure occurs in passing through the initial *monohydroxy* stage. Indeed, it is conceivable that under the extreme conditions of detonation the passage from 0 to 2 may be effected in a single molecular impact. The *dihydroxy* derivative would at once break down into carbon monoxide and hydrogen, *via* formaldehyde.

But when the oxygen supply is reduced below the equimolecular proportion, it is evident that the initial *monohydroxy* derivative cannot all be oxidised to the *dihydroxy* stage; some of it would, therefore, decompose, partly into acetylene and steam, and partly also into carbon, hydrogen, and steam, together with some methane.

In a similar manner the combustion of ethane would involve the rapid passage through *ethyl alcohol* to *acetaldehyde*, and *steam*, with subsequent decomposition of the aldehyde into carbon, hydrogen, methane, and carbonic oxide, with the proviso that a reduction of the oxygen supply below the equimolecular proportion would bring about in some measure the decomposition of the alcohol into ethylene and steam, &c., at Stage 1.

$$H_3\overset{0}{C}.CH_3 \rightarrow CH_3.\overset{1}{C}H_2OH \rightarrow CH_3.\overset{2}{C}H(OH)_2$$

$$\left\{\begin{matrix}C_2H_4+H_2O\\ 2C+2H_2+H_2O\end{matrix}\right\} \qquad CH_3.CHO+H_2O$$

$$\left\{\begin{matrix}CH_4+CO\\ C+2H_2+CO\end{matrix}\right\}$$

But the cases of ethane and ethylene are typical of all other hydrocarbons, so that it may be said that, in general, the mechanism of explosive combustion involves, (1) the initial formation and subsequent decomposition of hydroxylated (or "oxygenated") molecules; (2) in a sufficient supply of oxygen, the independent oxidation of the decomposition products; (3) in an insufficient oxygen supply, the subsequent breaking down of unsaturated hydrocarbons, interactions between carbon and steam, or between oxides of carbon, hydrogen, and steam, the final system depending on the amount of available oxygen, the temperature of the flame, and the rate of cooling.

Experiment V.

The influence of different rates of cooling of the flame on the final system may be illustrated by firing an equimolecular mixture of ethane and oxygen in two glass vessels, having approximately the same volume but widely different surface areas. For this purpose I have selected (1) a tube about 1 metre long and 2 cm. internal diameter, and (2) a globe of 8·5 cm. internal diameter. Both these vessels have the same volume (about 300 cc.), but the surface area of the tube is very nearly three times that of the globe. It is therefore to be expected that, in consequence of the more rapid cooling of the flame, there will be a greater accumulation of the primary combustion products in the case of the tube experiment. On comparing the results of the two explosions, it is at once evident that more water and less carbon have been produced in the case of the tube; moreover, the pressure ratio p_2/p_1, is 1·45 as compared with about 1·75 in the globe experiment, and an examination of the products would show that the lower ratio is accounted for by the much greater survival of acetylene, ethylene, and aldehydic products in the tube experiment. These facts, which are set forth in Table III., are in complete harmony with the hydroxylation theory.

Experiment VI.

The experiments I have so far shown you, refer more particularly to the initial period of "*inflammation*" in explosive combustion; that is to say, to the conditions ordinarily prevailing in hydrocarbon flames. The question may be asked whether or not the views I have advanced are applicable to the extreme conditions of "*detonation*" or of explosions under high initial pressures. The question may be put in the following form:—Is there any experimental evidence of discontinuity between "*inflammation*" and "*detonation*" as regards the nature and sequence of the chemical changes involved? or, Is the hydrocarbon attacked by oxygen in an entirely different way in explosive combustion at high pressures, or in the explosion wave, to what it is in ordinary flames? This question can, I think, best be answered by a consideration of the behaviour of an equimolecular mixture of ethane and oxygen under these extreme conditions.

It is difficult to set up detonation in this mixture; the gases must be fired at an initial pressure of about one and a-half atmosphere in a stout leaden coil of about one inch internal diameter. Even then, it is necessary to start the explosion wave in a special firing piece containing electrolytic gas under pressure. I therefore regret that, owing to the special arrangements requisite for success, it is not possible to make the experiment to-night. I will, however, give you the results obtained on detonating the mixture in my laboratory, but before doing so, I will carry out an experiment on the explosion of the gases at an initial pressure of fifteen atmospheres.

The cylindrical steel bomb on the table is part of an apparatus recently installed in the Fuel and Metallurgical Laboratories of the University of Leeds for investigations on gaseous explosions under high pressures. The bomb is about a foot long with an external diameter of four inches, and the central cylindrical explosion chamber is eight inches long by one inch in diameter. It has been tested by hydraulic pressure up to 2000 atmospheres, and has been repeatedly used for experiments with mixtures of hydrocarbons and oxygen at initial pressures of as much as forty atmospheres. The bomb is now connected, through a valve at the top, with a standard Bourdon gauge, and contains an equimolecular mixture of ethane and oxygen at a pressure of 15·8 atmospheres. The valve will now be closed, and the mixture fired by means of an electrical arrangement in the special firing piece.

All that is audible of the explosion is a sharp click, and on opening the valve connecting with the gauge again, the final pressure of the cold products of explosion is recorded. After applying the necessary correction for the "dead space" in the gauge connections, but the final "corrected" pressure is as nearly as possible 30·8 atmospheres, corresponding to a ratio $p_2/p_1 = 1·93$. I would now direct your attention to the tabulated results of a similar bomb experiment carried out a few weeks ago at Leeds at an initial pressure of twenty-five atmospheres, and also at the same time to those of another experiment in which the gases were detonated in a lead coil at an initial pressure of one and a-half atmosphere (see Table IV.).

In both these experiments carbon was deposited, and it is evident also that steam was formed. The ratio p_2/p_1 was as nearly as possible 2·0 instead of the 2·5 required by the theory of the preferential combustion of carbon. Moreover, a notable feature of the results is the presence of as much as 7 per cent of methane among the products of the experiment at twenty-five atmospheres; the fact that so much methane survived when all other hydrocarbons were battered to pieces during the explosion (no traces of either acetylene or ethylene being found in

the products) is a remarkable testimony to its relatively great stability at the highest temperatures of explosion flames. There is no evidence in these experiments of any real discontinuity between the chemical phenomena of ordinary "*inflammation*" and those of "*detonation*." The higher temperatures and more violent conditions in "*detonation*" are responsible for the more complete breaking down of unsaturated hydrocarbons, and a greater "unburning" of steam by carbon, but there is probably no difference as regards the mode in which the hydrocarbon is attacked by the oxygen in the two cases.

I therefore believe that, so far as our present knowledge goes, the views I have put forward afford a simple and consistent interpretation of hydrocarbon combustion, whether it be the slow flameless kind discovered by Davy, or the more complex phenomena of ordinary flames so wonderfully expounded by him, or finally the extreme conditions characteristic of the explosion wave.

I desire to acknowledge the devoted help rendered to me in the conduct of these investigations by the following research students of the Manchester University :—Messrs. R. V. Wheeler, W. E. Stockings, G. W. Andrew, Julien Drugman, and H. Henstock.

VOLUMETRIC METHOD FOR THE DETERMINATION OF ZINC.*

By WM. HERBERT KEEN.

(Concluded from p. 202).

To Determine Zinc in Ores.

Decompose 1 grm. of the sample in a beaker with hydrochloric acid, or if necessary with aqua regia. Evaporate to dryness, and if nitric acid has been added re-dissolve in hydrochloric acid and evaporate again. Dissolve in 15 cc. of hydrochloric acid (1·20), dilute with water, filter, and wash. Burn off the filter (unless it contains lead) in a platinum crucible, and treat with hydrofluoric and sulphuric acids—exactly as in a silica determination. Dissolve the residue in hydrochloric acid, and add to the solution. Usually this treatment of the residue is not necessary, as it rarely contains more than a few hundredths of a per cent of zinc. If lead sulphate is present in this residue, use a perforated crucible with an asbestos felt for a filter. Remove the filtrate after washing the residue thoroughly, and dissolve out the lead sulphate with a strongly ammoniacal solution of ammonium citrate. Wash with hot water, and then transfer the remaining residue, together with the felt, to an ordinary platinum crucible and treat with hydrofluoric acid as before, finally adding the hydrochloric acid solution of the remaining residue to the filtrate. (Advantage may be taken of the above steps to determine the lead in the same portion—the only changes necessary being to evaporate with sulphuric acid instead of hydrochloric, and to weigh the perforated crucible before and after treatment with the ammonium citrate, calling the difference lead sulphate). Neutralise the filtrate with ammonia, and again acidify, adding about 3 cc. of acid in excess for every 200 cc. of solution. Pass hydrogen sulphide through the solution to remove the copper group, and, having filtered out the precipitate thus obtained, heat until the free hydrogen sulphide has boiled off, and then add an excess of bromine water, and evaporate to about 50 cc. Precipitate the iron with ammonia, using a large excess, and washing with water containing ammonia. If the precipitate amounts to more than a few tenths of a per cent it should be dissolved and re-precipitated, and in case of large amounts of iron a third precipitation is sometimes necessary. Acidify the filtrate with hydrochloric acid, adding 3 cc. in excess. The solution is now ready for titration. unless manganese is present, if its volume does not exceed 150 to 200 cc. If it is of larger bulk than this, it should be evaporated until of approximately this volume, before titration. In the case of very large amounts of iron the sulphide of zinc should be separated from it just as described below when nickel is present, or, if preferred, the ether separation may be used.

When Manganese is present in the Ore.—If the iron is small in amount, add to the solution after evaporation, but before removing the iron, 5 grms. or more of potassium or sodium bromide. Make strongly ammoniacal, and stir for an hour by means of some such device as that used for the solution of steels in the determination of carbon. If no appliance of this sort can be had. the solution should be allowed to stand over-night at room temperature. The manganese and iron are completely precipitated, and should be filtered off, and washed with water containing ammonia. The filtrate should then be acidified as above and titrated. If the iron is present in large enough quantities to require re-precipitation, it should be removed before treatment with the bromide ; but if both the manganese and iron are precipitated together, as above, and it is desired to re-precipitate them, they should be dissolved in a mixture of hydrochloric and sulphurous acids, the solution boiled to expel the sulphurous fumes, and then oxidised with bromine water. The bromine should be boiled off as before, and the precipitation then repeated with the alkali bromide and ammonia. The amount of bromide may be varied without any effect on the titration. If it is desired to determine the manganese, it may be dissolved in sulphurous acid alone, and after solution is complete, nitric acid added, the nitrous fumes boiled out, and the determination completed by the bismuthate method.

Of course the manganese may be readily avoided by precipitating the zinc as sulphide from a slightly acid solution, and this is to be advised in the case of large amounts of manganese—also if any nickel is in evidence. The presence of nickel will be made known by a blue colour of the ammoniacal filtrate from the iron. If it is necessary to precipitate the sulphide of zinc to avoid these metals, the best plan is to evaporate the hydrochloric acid as first obtained to a small bulk in order to expel most of the free acid, dilute with a little water, and neutralise with sodium carbonate solution, using methyl orange as an indicator. The neutral point should be carefully obtained and then *ten drops* of hydrochloric acid added. Wash down the sides of the beaker, dilute to 200 cc., and pass hydrogen sulphide through the *cold* solution for an hour. Let the solution stand for several hours, or, if convenient, over night before filtering. Zinc sulphide precipitated in this way should filter out like so much sand. Put the paper containing the precipitate into a beaker and digest until dissolved in 10 cc. of hydrochloric acid diluted with water. Pass hydrogen sulphide for a few minutes to be sure that all the copper is precipitated, and then filter and wash thoroughly with hot water. Evaporate the filtrate after adding a slight excess of bromine water to oxidise any iron that may have been occluded by the zinc, and when it is reduced to a small volume add an excess of ammonia and boil. Filter, if necessary, and neutralise the filtrate with hydrochloric acid, adding 3 cc. in excess. Dilute to 150 cc. and titrate. This method is excellent if the conditions are just right, but my idea has been to avoid a precipitation of the zinc, if possible, and thus get rid of what may be a troublesome filtration. Accordingly, I have endeavoured, except in cases where nickel is present, to precipitate from the zinc all metals interfering with the titration.

Brasses.—Remove the tin, copper, and lead in the usual way—by solution in nitric acid, filtration of the metastannic acid, and deposition of the two latter metals by electrolysis. If it is certain that the copper is entirely removed, evaporate to dryness the nitric acid solution, which now contains only the zinc and perhaps a small amount of iron. Dissolve the residue in 10 cc. of strong hydrochloric acid and, after dilution, precipitate the iron with ammonia, being careful to boil long enough to insure a complete precipitation, as iron comes down very slowly when present in such small quantities. Filter and wash with dilute ammonia water and then with hot water. Neutralise

* *Journal of the American Chemical Society*, xxx., No. 2.

the filtrate with hydrochloric acid, add an excess of 3 cc., dilute to 150 cc., and titrate with the standard ferrocyanide solution. In the case of a manganese bronze, the only modification would be the treatment with alkali bromide, as described above under ores.

It is sometimes easier, in the case of brasses, to make the filtrate from the electrolysis ammoniacal and add colourless ammonium sulphide. Digest at a temperature near the boiling-point for about an hour, allow to settle and filter, keeping as much of the precipitate in the beaker as possible. When the liquid has run through the funnel, replace the filtrate beaker by the one containing the precipitate and pour dilute hydrochloric acid over the filter, allowing it to run through on to the main bulk of the precipitate. Wash the filter once or twice and heat the solution until the zinc is dissolved. Pass a current of hydrogen sulphide for a few minutes and filter out any small traces of copper that may be precipitated as sulphide. Oxidise the filtrate with bromine water and evaporate to a small volume, finally precipitating the small amount of iron and finishing as before.

Aluminium Alloys containing Zinc.—Aluminium does not affect the ferrocyanide, and so the natural idea would be to dissolve in hydrochloric acid and proceed directly with the titration as soon as solution was complete. But iron is almost always present in such alloys to a considerable amount, and hence the necessity for a more roundabout method. Dissolve 1 grm. in either nitric or hydrochloric acid. Add a few crystals of citric acid, make ammoniacal, and heat to boiling. Remove from the source of heat and add a little colourless ammonium sulphide. Allow to settle and then filter, being careful to wash out the last traces of citric acid with a wash water containing a little ammonium sulphide. The precipitate will consist of sulphide of zinc, iron, and copper metals. Treat it exactly as described for brasses under similar conditions. If desired, the metal may be dissolved in hydrochloric acid and the zinc precipitated as sulphide from a slightly acid solution just as when it is required to separate it from nickel.

In general, any one working intelligently, realising the final conditions, and knowing something of the material in hand, will find no difficulty in following out the plan of this method.

MISCELLANEOUS.

Institute of Chemistry.—*April Examinations*, 1908.—Of twelve candidates who presented themselves for the Intermediate Examination, the following nine passed: F. S. Aumonier, T. Blackadder, B.Sc. (St. Andrews), R. H. Findlater, G. A. Freak, B.Sc. (Lond.), C. Harris, J. Kenyon, B.Sc. (Lond.), W. N. Morley, O. J. Patrick, and A. R. Smith, B.Sc. (Manc.) In the Final Examination for the Associateship, of seven candidates who presented themselves in the Branch of Mineral Chemistry, the following four passed: W. Colet Birch, B.A. (Cantab.), J. Gibbon, E. S. Poole, B.Sc. (Lond.), and W. E. F. Powney. Three candidates presented themselves in Organic Chemistry, and passed: G. H. Frank, B.Sc. (Leeds), F. W. Linch, and W. W. Reed, B.Sc. (Wales). Of six candidates in the Chemistry of Food and Drugs, &c., four passed: L. Clement, B.A., (Cantab.), J. C. Cowap, B.Sc. (Vict.), J. W. Haddon, B.Sc (Vict.), and D. R. Wood. Four candidates presented themselves for examination for the Fellowship, and one passed in Metallurgical Chemistry: T. H. Byrom.

MEETINGS FOR THE WEEK.

MONDAY, 4th.—Royal Institution, 5. General Monthly Meeting.
—— Society of Chemical Industry, 8. "Manufacture of Sodium Nitrite," by G. T. Morgan. "Some Simple and Mixed Esters of Cellulose—The Alkaline Decomposition of Nitro-derivatives of Cellulose and other Carbohydrates," by W. Smith, jun. "The Mechanism of Filtration," by E. Hatschek. "Metanil Yellow—Its Use as a Selective Indicator," by E. Linder. "Conversion of Oleic Acid into Stearic Acid," by J. Lewkowitsch.

TUESDAY, 5th.—Royal Institution, 3. "The Development of the Modern Turbine and its Application," by Gerald Stoney, M Inst.C.E., &c.

WEDNESDAY, 6th.—Royal Society of Arts, 8. "The Gramophone, and the Mechanical Recording and Reproduction of Musical Sounds," by Lovell N. Reddie.
—— Society of Public Analysts, 8. "Examination of Oil of Turpentine and Turpentine Substitutes," by J. H. Coste. "Estimation of Ferrocyanide in Crude Commercial Products," by H. G. Colman. "Studies in Steam Distillation III., The Fatty Acids," by H. D. Richmond. "New Method for Milk Testing, and some Remarks on the Sydney Supply," by W. M. Doherty.

THURSDAY, 7th.—Royal Institution, 3. (The Tyndall Lectures). "Mendelian Heredity," by William Bateson, F.R.S., &c.
—— Chemical, 8.30. "Interaction of Diazonium Salts with Mono- and Di-hydric Phenols and with Naphthols," by K. J. P. Orton, and R. W. Everatt. "Condensation of Benzoin with Methyl Alcohol," by J. C. Irvine and D. McNicoll. "Mutual Solubility of *a*-Methylpiperidin and Water," by O. Flaschner and B. MacEwen. "Melting-points of the Anilides, *p*-Toluidides, and *a*-Naphthylamides of the Normal Fatty Acids," by P. W. Robertson. "Refraction and Dispersion of Triazo-compounds" and "Dissociation Constants of Triazoacetic and *a*-Triazopropionic Acids," by J. C. Philip. "Absorption Spectrum of Camphor," by W. N. Hartley. "Viscosity of Solutions." by C. E. Fawsitt. "Action of Fused Potassium Hydroxide and of Hydrogen Peroxide on Cholesterol," by R. H. Pickard, and J. Yates. "Fermentation of Mannose and Fructose by Yeast Juice," by A. Harden and W. J. Young. "Volumetric Estimation of Silver," by W. R. Lang and J. O. Woodhouse. "Constituents of Olive Leaves," and "Constituents of Olive Bark," by F. B. Power and F. Tutin.

FRIDAY, 8th.—Royal Institution, 9. "Ice and its Natural History," by J. Y. Buchanan, F.R.S., &c.
—— Physical, 8. "A Modified Theory of Gravitation," by C. V. Burton. "An Examination of the Formulæ for the Grading of Cables," by C. S. Whitehead. "Illustrations of Geometrical Optics," by R. M Archer.

SATURDAY, 9th.—Royal Institution, 3. "Chile and the Chilians," by C. F. Scott Elliot, M.A., &c.

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THE CHEMICAL NEWS.

Vol. XCVII., No. 2528.

THE DECOMPOSITION OF DOLOMITE.

By NICHOLAS KNIGHT.

The dolomites of Iowa and other sections of the country, belonging to the Niagara period of the Upper Silurian, in the course of centuries apparently undergo decomposition. The rock loses its massive structure and becomes crumbly and mealy in appearance. In the vicinity of Mount Vernon, Iowa, the top layer to the depth of 3 or 4 inches seems to be quite thoroughly disintegrated and powdery. The same phenomenon is observed in lower strata where a layer projects, by which it is especially exposed to the elements. A similar disintegration is observed in many other localities.

It seemed reasonable to suppose that some constituent or constituents of the rock are more soluble than the others, or more easily acted upon by atmospheric agencies. The analysis of a more or less disintegrated air-dried specimen resulted as follows :—

SiO_2	0·56 per cent
Fe_2O_3 and Al_2O_3	0·74 ,,
$CaCO_3$	48·43 ,,
$MgCO_3$	50·56 ,,
	100·09

The analysis of a typical massive specimen gave :—

SiO_2	0·83 per cent
Fe_2O_3 and Al_2O_3	0·59 ,,
$CaCO_3$	53·62 ,,
$MgCO_3$	44·96 ,,
	100·00

It is thus seen that about 5 per cent of the calcium carbonate has been removed, and the magnesium carbonate is relatively stable. Other portions of the rock would doubtless show greater disintegration.

Immediately above the disintegrated layer referred to are found portions of what appears like a ferruginous clay. In all likelihood it formerly existed as a distinct layer, but was largely removed by the ice-sheet. It has accumulated in various cavities and depressions in the rock. This formation is quite widely extended. In North-East Iowa it is several feet in thickness, and in South-Western Wisconsin, on broad uplands, where it has been but little disturbed by the ice-sheet, it has a thickness of 13 feet.

An analysis of the ferruginous clay resulted as follows :—

SiO_2	16·68 per cent
Fe_2O_3	60·87 ,,
Al_2O_3	6·18 ,,
CaO	0·22 ,,
MgO	0·03 ,,
H_2O	17·14 ,,
	101·12

This clay probably resulted from the dolomite by the slow solution of the calcium and magnesium carbonates. The typical specimen of the rock referred to above contained 0·25 per cent Al_2O_3 and 0·34 per cent Fe_2O_3; therefore the alumina seems to have been removed much more rapidly than the ferric oxide.

If this deposit resulted from the decomposition of dolomite it must have been very slow in forming, and the accumulation of as great a quantity as 13 feet must have required a very long time.

Our thanks are due to Mr. Merle S. West for making the analyses described in the foregoing.

Cornell College, April 2, 1908.

A METHOD FOR THE SEPARATION OF IRON FROM INDIUM.

By F. C. MATHERS.

One of the most difficult steps in the purification of indium is its separation from iron. Winkler (*Journ. Prakt. Chem.*, 1865, xciv., 1) obtained a separation by the fractional precipitation of the sulphide, the indium sulphide being less soluble than the iron sulphide. A more satisfactory method was devised by Bayer (Bayer, *Liebig's Annalen*, 1871, clviii., 372), who treated a solution of the mixed chlorides with sodium sulphite. Basic indium sulphite is precipitated from this solution upon boiling. The precipitate, after filtration, was dissolved in a solution of sulphurous acid, and basic indium sulphite was again precipitated by boiling. This solution and re-precipitation was repeated several times to completely purify the indium. The Bayer method was tested in this laboratory, but gave unsatisfactory results. Weselsky (*Journ. Prakt. Chem.*, 1865, xciv., 443) treated the chlorides of indium and iron with sulphur dioxide or sodium thiosulphate, and then with barium carbonate, which precipitated indium hydroxide, together with traces of iron and zinc. Meyer (*Liebig's Annalen*, 1869, cl., 137) treated the material that contained indium and iron with sodium carbonate until neutral and then with a solution of potassium cyanide until the precipitate that first formed was re-dissolved. The solution thus formed was diluted with ten volumes of water and was boiled. This decomposed the potassium indium cyanide and indium hydroxide was precipitated, while the iron remained in solution as potassium ferri- or ferro-cyanide. This method was found, upon trial, to give fair results. The indium, however, is not completely precipitated by boiling, considerable amounts of it being found in the filtrate. The precipitate is very gelatinous, difficult to wash, and often passes through the filter-paper before the washing is completed. For these reasons the method is not satisfactory. Some quantitative results obtained in this laboratory with the Weselsky method follow :—

Indium oxide present (grm.)	0·0320	0·0515
Indium oxide precipitated by dilution and boiling (grm.)	—	0·0528 or 96·8 per cent
Indium oxide precipitated from the filtrate with ammonium hydroxide (grm.)	0·0022 or 6·8 per cent	0·0014 or 2·5 per cent

Dennis and Geer (*Journ. Am. Chem. Soc.*, 1904, xxvi., 437) have proposed the removal of the iron by extracting the ferric sulphocyanate with ether. This method has been applied to the removal of iron from nickel, cobalt, copper, aluminium, &c. Indium sulphocyanate, however, is quite soluble in ether, and for this reason indium is always present with the iron in the ether extract. The labour involved in recovering the indium thus dissolved constitutes a serious drawback in this method, which is otherwise very satisfactory and yields an indium that is free from iron.

Several other methods have been suggested for the separation of iron and indium, but those cited above seem to have been the ones most generally used and to have been the most satisfactory.

The method here proposed for the removal of iron from indium is the precipitation of iron from nitroso-β-naphthol. This reagent (Ilinski and Knorre, *Ber.*, 1885, xviii., 2728; Knorre, *Ber.*, 1887, xx., 283) quantitatively precipitates cobalt, copper, and iron, but does not precipitate aluminium, lead, zinc, or nickel. Experiment showed that indium also was not precipitated, and this led to the development of the following method of separation :—

A solution of the indium chloride or sulphate containing a small quantity of iron was evaporated to a volume of 20 to 25 cc., was neutralised with ammonium hydroxide, and then an equal volume of 50 per cent acetic acid was added. The iron in these solutions was precipitated with nitroso-β-naphthol dissolved in 50 per cent acetic acid. The solution may be either hot or cold when precipitated, but it should stand several hours before filtering, and should be cold when filtered. The residue is washed with 50 per cent acetic acid and finally with water. Before using this method the bulk of the iron must be removed by some other method. Since the precipitate of iron with nitroso-β-naphthol is very bulky, 0·05 grm. of iron is about the maximum quantity that can easily be handled on a 12 mm. filter-paper. The indium precipitated by electrolysis from a solution containing indium sulphate and quite large amounts of ferric sulphate and strongly acidulated with sulphuric acid, contains only small amounts of iron. This metal can then easily be freed from the iron that it still contains by precipitating the iron with nitroso-β-naphthol. Colorimetric analysis of the indium, after the precipitation of the iron by this method, showed that the content of iron was very low. This small amount of iron (Stokes and Cain, *Journ. Am. Chem. Soc.*, 1907, xxix., 409) could easily have been introduced into the solution during evaporation by the dust from the air. Quantitative determinations of the iron remaining in the indium gave the following results :—

Indium oxide taken (grm.)	0·3148	0·1738	0·2184	0·3061	0·2142
Ferric oxide added (grm.)	0·0328	0·0262	0·0197	0·0262	0·0262
Nitroso-β-naphthol used (grm.)	5·0	4·0	3·0	2·5	2·5
Ferric oxide still present in the indium oxide (grm.)	Less than 0·00005			Less than 0·0001	Very faint red

Some indium remains in the residue with the iron and a second precipitation will not remove all of it. The indium in these residues can easily be detected with the spectroscope. The total quantity of indium that is lost in these iron residues is, however, quite small, as is shown by the following data :—

Indium oxide taken (grm.)	0·3061	0·1520	0·2142
Ferric oxide added (grm.)	0·0262	0·0262	0·0262
Ferric oxide obtained from first precipitation (grm.)	0·0286	0·0283	0·0281
Second precipitation (grm.)	0·0273	0·0273	0·0266
Indium oxide in ferric oxide in first precipitation (grm.)	0·0024	0·0021	0·0019
Second precipitation (grm.)	0·0011	0·0011	0·0004

—*Journal of the American Chemical Society*, xxx., No. 2.

New Type of Compounds of Sulphur with certain Iodides.—V. Auger.—When sulphur and iodoform are dissolved in the smallest possible quantity of warm carbon disulphide, and the solution is cooled, pale yellow crystals separate out. They have the formula $HCI_3.3S_8$. This method of preparing molecular compounds of sulphur and iodides can be applied to other iodides, both organic and inorganic, and the products appear to have the general formula $RI_n.nS_8$. The author has prepared the following compounds :—$HCI_3.3S_8$, $CI_2CI_2.4S_8$, $AsI_3.3S_8$, $SbI_3.3S_8$. —*Comptes Rendus*, cxlvi., No. 9.

THE ESTIMATION OF IRON BY POTASSIUM PERMANGANATE AFTER REDUCTION WITH TITANOUS SULPHATE.

By H. D. NEWTON.

KNECHT (*Ber.*, xxxvi., 166) was the first to point out and recommend the use of titanium sesquioxide and its salts in volumetric operations where a rapid and powerful reducing agent is required. Somewhat later the same author in collaboration with E. Hibbert (*Ber.*, xl., 3819) published a method for the direct titration of ferric chloride by a standard solution of titanous chloride, using potassium sulphocyanate as an indicator, the reaction between the two salts taking place according to the following equation : — $FeCl_3 + TiCl_3 = FeCl_2 + TiCl_4$. According to these authors, the above method yields excellent results, and rapidly. The only precautions necessary are that the solution of titanous chloride, being naturally very sensitive to the action of atmospheric oxygen, must, after being boiled in presence of marble to expel occluded oxygen, be kept under a constant pressure of hydrogen. It has been found, however, that even with such precautions the standard of the solution gradually changes, and must be checked from time to time against known amounts of ferric iron.

The present investigation was undertaken for the purpose of adapting the well known and accurate method of titration with standard potassium permanganate to the determination of ferrous salts, after reduction has been effected by a titanous salt according to the excellent and rapid method of Knecht.

It has been shown in a former paper that bismuth oxide completely oxidises titanous sulphate while having no appreciable effect on salts of ferrous iron (*Am. Journ. Sci.*, xxiii., 365; CHEMICAL NEWS, xcvi., p. 148). So the plan of this work has been to reduce the iron by titanous sulphate, oxidise the excess of titanous sulphate by bismuth oxide, and titrate the remaining ferrous salt by permanganate.

A solution of titanous sulphate of convenient strength was made up by mixing 20 grms. of commercial titanic acid, in two portions, with three times its own weight of a mixture of sodium and potassium carbonates, and fusing in a platinum crucible until all the titanic acid was converted into the soluble alkali titanates. The melt obtained in this manner, after being finely ground, placed in a platinum dish, and treated with hot concentrated sulphuric acid (which soon effected solution) was cooled, diluted a little, and filtered. To these concentrated solutions of titanium sulphate, zinc was added until reduction was complete, and while there was some zinc left in the flask the solution was quickly filtered through a platinum cone into about 2 litres of freshly distilled water contained in a small reservoir, the latter being set up and connected with a burette and hydrogen generator as described by Knecht and Hibbert (*loc. cit.*).

A test solution of ferric sulphate was prepared by treating ferrous ammonium sulphate with oxalic acid, drying, and igniting the resulting ferrous oxalate, dissolving the ferric oxide thus formed with concentrated hydrochloric acid, and converting the ferric chloride to sulphate by digesting with concentrated sulphuric acid. After diluting and filtering, the solution was made up to known volume and standardised by drawing from a burette into 50 cc. flasks several portions, reducing each by a definite amount of zinc of known iron content, cooling, pouring into a litre of cold distilled water, and immediately titrating with tenth normal potassium permanganate.

In the following table are recorded results obtained by effecting the reduction of carefully measured amounts of the ferric sulphate solution by addition of an excess of titanous sulphate in the cold, destroying this excess by treating with a little bismuth oxide, filtering from the excess of bismuth oxide, and reduced bismuth into about a litre of cooled distilled water, and titrating with permanganate.

$Fe_2(SO_4)_3$.	$KMnO_4$.	Fe_2O_3 taken.	Fe_2O_3 found.	Error.
Cc.	Cc.	Grm.	Grm.	Grm.
20	13·46	0·1063	0·1064	+0·0001
20	13·42	0·1063	0·1060	−0·0003
20	13·44	0·1063	0·1062	−0·0001
20	13·44	0·1063	0·1062	−0·0001
20	13·41	0·1063	0·1060	−0·0003
30	20·18	0·1594	0·1594	—
30	20·20	0·1594	0·1596	+0·0002
30	20·20	0·1594	0·1596	+0·0002
30	20·22	0·1594	0·1598	+0·0004
30	20·19	0·1594	0·1595	+0·0001
40	26·92	0·2127	0·2127	—
40	26·90	0·2127	0·2125	−0·0002
40	26·90	0·2127	0·2125	−0·0002
40	26·93	0·2127	0·2128	+0·0001
40	26·90	0·2127	0·2125	−0·0002

In later experiments it was found that the bismuth oxide failed to oxidise the sesquioxide of titanium when there was an appreciable amount of hydrochloric acid present in solution. Therefore it is advisable if the original solution is made with hydrochloric acid, to evaporate to dryness, and convert the chloride to sulphate by use of concentrated sulphuric acid. Upon addition of the sulphuric acid a white pasty mass of basic ferric sulphate is formed which rapidly goes into solution on diluting with water and warming. As titanous sulphate prepared in the above manner always contains some iron, it is necessary to make a correction for this, by treating with bismuth oxide an amount of the solution equal to that used, filtering, and running in potassium permanganate to colour. This correction should not amount to more than 0·1 cc. when working with 0·3 grm. of ferric oxide.

If these simple precautions be taken, ferric iron may be determined with rapidity and exactness by reduction with titanous sulphate, and subsequent titration with potassium permanganate.—*American Journal of Science*, xxv., p. 343.

THE INTERACTION OF ALUMINIUM POWDER AND CARBON.*

By FRANK E. WESTON, B.Sc., and H. RUSSELL ELLIS, B.Sc.

In attempting to remove the grease with which aluminium powder is coated by gently heating, it was noticed that a black deposit was formed on the surface of the powder, accompanied by an evolution of heat with incandescence; as the temperature of heating was not above 400° C., it was thought probable that the aluminium powder had attacked the vapour produced from the grease, with the production of a carbide of aluminium differing from that formed by Moissan in the electric furnace at a very high temperature. (A gas with odour of acetylene was evolved in treating a portion with water). Very little information on the direct union of aluminium and carbon, without the use of the electric furnace, is available, and even that which has been published is vague, and in some cases contradictory. Moissan states ("The Electric Furnace," 1904, p. 235, in a footnote): —"According to Mallet aluminium does not combine with carbon; on the other hand, Franck, by calcining a mixture of aluminium and lampblack, obtained a metallic substance yielding hydrogen contaminated with acetylene when treated with hydrochloric acid" (see also *Bull. Soc. Chim.*, 1894, [3], xi., p. 439). Mallet's statement need not be considered in view of the fact that fine aluminium powder was not used or procurable, and for a similar reason the amount of carbide produced by Franck was small.

Franck (*Chem. Zeitung*, 1898, p. 236) prepared a small quantity of aluminium carbide by heating aluminium powder in carbon monoxide or carbon dioxide, and confirmed the experiments of Guntz and Moissan (*Comptes Rendus*, 1897, cxxiv., No. 4). He also made aluminium react with lampblack, producing a body which evolved a large amount of methane with water.

Fritz Fichter (*Zeit. Anorg. Chem.*, 1907, liv., p. 322), using a mixture of aluminium powder and soot, prepared an impure aluminium nitride as follows:—A mixture of aluminium powder with 4 to 5 per cent of soot is made and heated to a high temperature; it is then exposed to the air, when a vigorous action takes place, producing a fairly large yield of aluminium nitride.

Kusnetzkoff (*Ber.*, 1907, xl., p. 2871) showed that aluminium at temperatures near its melting-point decomposes CH_4, C_2H_6, C_2H_4, and C_2H_2 completely into their elements. The H and part of the C are obtained in the free state, whilst the remainder of the carbon forms aluminium carbide.

Matignon (*Comptes Rendus*, 1907, cxlv., No. 17) states Berthelot has shown that a large disengagement of heat takes place when aluminium and carbon react; and, therefore, since the reaction is exothermic, combination ought to take place without the aid of an electric furnace. Matignon showed that the two elements would combine when heated in a Perrot furnace, forming an olive-green or yellow product. He used lampblack, and obtained an intimate mixture by working the two together with terebenthene, the proportion of lampblack to aluminium being 24 to 70 or 140; Al_4C_3 requires 24 of carbon to 72 of aluminium. When the large excess of Al was used the action could be started by igniting the mixture in one place, when it spread throughout the mass. The product gave on treating with water a gas consisting of 96·36 per cent CH_4 and 3·36 per cent H. As will be shown later by the authors, the product of reaction must have contained nitride.

In a letter to the CHEMICAL NEWS, November 29, 1907, the authors call attention to the fact that a mixture of aluminium powder and wood charcoal could be made to react with a fuse of Mg and BaO_2, similar to the ordinary thermite reaction. The authors now present in this paper the results of their investigations on the interaction of aluminium powder with wood charcoal, sugar charcoal, and graphite respectively. With each kind of carbon it was found possible to prepare a mixture with aluminium powder which, when started with a fuse of Mg powder and BaO_2, would react with vivid incandescence throughout the mass, similarly to the ordinary thermite reaction, the action being most pronounced in the case of wood charcoal. Mixtures which would not react with a fuse were found to do so when placed in a muffle furnace and heated to temperatures varying from 400° C. to 1100° C. In some cases it was found that in heating the mixture in a closed Hessian crucible to dull redness, and then withdrawing the crucible and opening to the air, vigorous action took place throughout the mass, starting at the surface and proceeding downwards. In all cases the product of the reaction was found to contain the following: Aluminium carbide, aluminium nitride, aluminium oxide, carbon, and aluminium. The percentage of Al_2O_3 produced varied from 10 to 55, not only in the different mixtures, but in different parts of the same mixture. All the products gave with water mixtures of CH_4 and H, the former produced by the action of water on the aluminium carbide, Al_4C_3, viz., $Al_4C_3 + 12HO = 4Al(OH)_3 + 3CH_4$, whilst the H was produced by the action of free Al in water in the presence of the NH_3 liberated by the action of water on the aluminium nitride (see later). Since CH_4 was the only hydrocarbon obtained either by the action of water or hydrochloric acid, the authors conclude that the only carbide formed in the reactions mentioned is the one described by Moissan, viz., Al_4C_3. (This result confirms that of W. H. Patterson, CHEMICAL NEWS, December 20, 1907, who prepared aluminium carbide in the electric furnace at different temperatures, and could only obtain the carbide Al_4C_3).

The authors are of opinion that in all the reactions between aluminium and carbon mentioned above, the air

* A Paper read before the Faraday Society, April 28, 1908.

plays a most important part; the first action being the oxidation of the carbon to CO and CO_2,* thus producing sufficient heat to cause the oxidation of the Al powder to Al_2O_3, and this latter reaction raising the temperature sufficiently high to cause combination between the aluminium and the carbon, as well as the aluminium and nitrogen, the nitrogen coming from both the atmosphere and the occluded gases in the carbon. That the reason assigned is most probable follows from the following experimental facts :—

1. The reaction was most vigorous in the case of wood charcoal. All the mixtures of Al and wood charcoal were extremely porous, and hence contained plenty of air; also the volume of the carbon was greater proportionately to the aluminium in these mixtures than in the others; moreover, the wood charcoal contained ten times its own volume of occluded gases consisting of O and N.

2. Mixtures of aluminium and carbon which reacted with a fuse, when exhausted with a Töpler pump and heated to a full red heat, underwent very slight change (see analysis, *prox.*).

3. Mixtures of Al and C (all kinds) when heated in a current of air, reacted before temperature had risen to a visible red heat, and continued throughout the mass. The products always contained carbide, nitride, and oxide, the two latter predominating under these conditions.

Experimental.

Series I.—*Aluminium and Wood Charcoal.*

The aluminium powder used was the finest obtainable from the British Aluminium Company. It was freed from its adherent coating of grease by extraction with ether and dried in a steam oven. The wood charcoal used was first heated for an hour in a closed tin at a temperature of about 1000° C.; allowed to cool, powdered, and sieved. After passing through a 40,000-mesh sieve, it was again separated into a fine and coarse portion by means of a Goreham-Griffin theorometer to which a special receiver was fitted to collect the fine powder; this fine powder was used in the experiments. On igniting a weighed portion of the wood charcoal in a muffle, a brown residue was obtained which was 3 per cent of the charcoal taken.

Three sets of mixtures were made up, having compositions represented by the following :—(1) 4Al to 3 C; (2) 4 Al to 6 C; (3) 8 Al to 3 C.

Mixture containing 4 Al *to* 3 C :—

1. The mixture was placed in a Hessian crucible and a fuse of Mg powder and BaO_2 powder placed on top; into this a piece of Mg ribbon was put and lighted. The reaction commenced slowly at first, but then proceeded with increasing vigour and incandescence throughout the mass. It was found that the reaction took place best when the fuse was spread all over the surface, thus showing that a good heat supply must be available in order to start the action.

2. The mixture was placed in a porcelain basin and gently heated over a Bunsen burner. In five minutes a slight glow appeared at the bottom of the basin and slowly spread throughout the mass, and on reaching the upper surface bright incandescence took place, due to the burning of the Al in air. On cooling and examining the contents of the basin, a white layer one-sixteenth inch thick completely covered the top, whilst below was found a greyish black solid mass; no Al was visible.

3. The mixture, in a Hessian crucible, was placed in the front part of the muffle furnace and heated to about 400° C. After a few minutes a glow appeared on the top, when the crucible was withdrawn; the reaction spread throughout the mass slowly.

4. The mixture was placed in a Hessian crucible, covered with a piece of asbestos cardboard, and then tightly packed with a layer, three-quarter inch thick, of finely powdered MgO. Two crucibles were prepared and placed at the back of the muffle, which was at a temperature of between 1000° and 1100° C. One was left there two hours; the other was withdrawn at the end of five minutes and immediately opened; the contents instantly became incandescent.

Mixture containing 4 Al *to* 6 C.—This mixture could not be made to react with a fuse. The mixture was placed in a Hessian crucible and covered as before and heated half-an-hour at a temperature of about 1000° C. On cooling the resulting mass was found to be soft and easily removable; at the top was found a very thin layer of Al_2O_3.

Mixture containing 8 Al + 3 C.—This mixture would not react in the cold with a fuse, but on heating in a crucible over a Bunsen the reaction took place easily. The mixture, placed in a Hessian crucible and covered as before, was heated for fifteen minutes at about 1000° C. After five minutes CO appeared at a crack near the bottom of the crucible and burnt, and the crucible could be seen getting visibly hotter; CO also burnt on the top of the crucible. On cooling and opening the contents of the crucible were quite hard and crystalline, and at the top and near the crack a very thin layer of Al_2O_3 was found.

The products obtained in all the above experiments were more or less greyish-black in colour, and the core contained in all cases distinct yellowish crystals.

In no case were the contents of the crucibles the least disturbed, showing that very little gaseous products had been produced, but that combination between the carbon and aluminium had taken place.

On treating the powdered residue with water no action took place for some five to ten minutes; after this a gas was slowly evolved, but at a gradually increasing rate, and in the cases where only a small quantity of water was used a very violent evolution of gas took place after a short time and the flask became very hot. Using a large excess of water, no heating took place, and the gas was steadily and very slowly evolved for several weeks (in one case six weeks, another twelve, &c.). The solutions smelt strongly of NH_3, especially after a day or two, and the gas had a slight odour of acetylene and burnt readily with a slight whitish flame. The gas was fully analysed, and contained less than 0·2 per cent of acetylene or other unsaturated hydrocarbons (see analyses). When generating flask was placed in hot water the action was immediately vigorous. The solid products, therefore, contained carbide and nitride as well as aluminium, &c. After several attempts at analysing the solid the following process was adopted, which, although not of a high degree of accuracy, is sufficiently accurate to show the difference between the constitution of the products obtained in the various reactions.

Method of Analysis of the Crude Product of Reaction.

1. *Estimation of Free Aluminium.*—0·1 to 0·3 grm. of the substance, after crushing and sieving through 40,000 sieve, was placed in ice-cold conc. HCl, kept well cooled in ice and salt, and thoroughly and continuously shaken for twenty minutes (see Moissan, "Electric Furnace"). The evolution of gas was fairly rapid at first, but at end of ten minutes was almost over. The solution was diluted with ice-cold water, filtered at the pump, washed with ice-cold water, and the dissolved Al in the filtrate estimated in the usual manner with NH_4OH. This treatment dissolved free Al, but left undissolved the whole of the carbide, nitride, and alumina. Comparative tests were made.

2. *Estimation of Free* C, Al_2O_3, Al_4C_3, *and* AlN.—This involved two distinct processes, viz. :—

A. About 2 grms. of substance—ground, &c., as in 1—are boiled in a conical flask for two to three hours with equal vols. of conc. HCl and water (100 cc.). The prolonged boiling is necessary in order to dissolve that carbide and nitride which are protected with a

* Pring (*Journ. Chem. Soc.*, October, 1905, p. 1521), in preparing aluminium carbide in the electric furnace, considers it is formed by action of Al on CO and CO_2 from the furnace gases.

layer of Al_2O_3. H and CH_4 escape rapidly at first and then slowly for a time. At end of time stated the solution is diluted and filtered at the pump through a tared filter-paper and residue well washed—washing collected with original filtration. The residue, which is black, is dried and weighed to constant weight. This residue consists of C, H_2O_3, and traces of SiO_2 (found to be very small and hence neglected); it was placed in muffle and burnt till quite white and to constant weight. This process burns off the C. It was observed early in the work that when the boiling with the HCl was not prolonged the residue gained weight on ignition, showing the presence of unacted upon carbide and nitride, viz., $Al_4C_3(144) \rightarrow 2Al_2O_3(204)$ and $2AlN(82) \rightarrow Al_2O_3(102)$. The filtrate contained $AlCl_3$ (and traces of $FeCl_3$) derived from action of HCl in the free Al, the Al_4C_3, the AlN, as well as some of the Al_2O_3 (see Note). It was evaporated to dryness in a water-bath, re-dissolved in water, and again evaporated to dryness with NH_4OH, and then ignited in the muffle in a tared basin; the Al_2O_2 thus obtained was weighed. The residue obtained was always found to be quite white, though it contained traces of Fe_2O_3 which were neglected in the estimation.

B. *Estimation of the* AlN.—The principle used was the decomposition of the nitride by HCl and estimating volumetrically the amount of NH_3 produced. A weighed quantity of the powdered substance was heated in a flask with HCl, as in 2 A, for two to three hours; the flask B was then fitted up as shown in a diagram; excess of strong KOH solution was then run in through the funnel (D), and the evolved NH_3 collected in standard H_2SO_4 in C. It will be noticed that NH_3 free air is aspirated through the apparatus during the whole time of the distillation; this ensured a regular and steady ebullition in the flask A; a few drops of phenol-phthalein solution was always placed in B before fixing up in order to indicate when excess of KOH had been added. A contains dilute H_2SO_4. Flasks B and C were easily removed, and replaced without disturbing remainder of apparatus. Blank experiments were carried out with the apparatus as well as tests with known strengths of NH_4OH solution in order to test its accuracy.

Contents of Flask B ..	1.	100 cc. concentrated KOH
	2.	50 ,, ,,
	3.	5 cc. N/10 NH_4OH and excess KOH
	4.	5 ,, ,, ,,
Contents of Flask C ..	1.	10 cc. N. H_2SO_4
	2.	20 ,, ,,
	3.	5 ,, ,,
	4.	10 ,, ,,
Acid found in C after distillation ..	1.	10 ,, ,,
	2.	20 ,, ,,
	3.	45 cc. N/10 H_2SO_4.
	4.	95 ,, ,,

Method of Calculating Composition of Product.

1. By direct estimation is obtained weight of Al, C, and AlK.
2. By direct estimation is obtained weight of Al_2O_3 produced from Al, AlN and Al_4C_3, and Al_2O_3.
3. Let X be weight of substance taken and
   Let X^1 be weight of (Al + C + AlN) found.
   Then $X - X^1$ is weight of Al_4C_3 and Al_2O_3 in original substance.
   Let x be weight of Al_2O_3 found by experiment produced from Al, AlN, Al_4C_3, and Al_2O_3,
   And y be calculated weight of Al_2O_3 produced from X^1 parts of (Al + C + AlN);
   Then $x - y$ is the weight of Al_2O_3 produced from $(X - X^1)$ parts of (Al_4C_3 and Al_2O_3).
   When Al_4C_3 (144) is converted into $\rightarrow 2Al_2O_3$ (204), an increase of 60 parts by weight corresponds to 144 Al_4C_3.

Hence an increase of $[(X - X^1) \backsim (xy)]$ parts by weight corresponds to $\frac{144[(X - X^1) \backsim (x - y)]}{60}$ parts of Al_4C_3 (say = Z), and hence also weight of $Al_2O_3 = (X - X^1) - Z$.

Note on the Solubility of Al_2O_3 *in* HCl.

Statements as to the solubility of Al_2O_3 in HCl differ considerably. As in our method of analysis we wished for confirmatory evidence as to the solubility of Al_2O_3 under the conditions there carried out, the following tests were performed:—

Test 1.—Anhydrous Al_2Cl_6 was heated in the muffle furnace at a temperature of 1000°—1100° C. for five hours, thus converting it into Al_2O_3. A weighed quantity of this Al_2O_3 was boiled for three hours with conc. HCl, allowed to stand three hours, filtered, and residue well washed, &c. The Al in filtrate was estimated by NH_4OH in usual manner:—

Weight of Al_2O_3 used	2·4085 grms.
Weight of insol. portion in HCl..	0·6900 ,,
Weight of soluble	1·7026 ,,
Total..	2·3926 ,,

Test 2.—A layer of Al powder (purified) about one-eighth inch deep was spread over a porcelain basin and inserted into the hottest part of the muffle, which was left open. The Al commenced to burn and was brought to the front of the muffle, and here continued to burn with intense light and heat. The residue was greyish-white, not pure white, whilst a fairly large amount of black substance was present. This was boiled for three hours with 2N . HCl to remove any nitride (see analysis of nitride in Al powder burnt in air) and free Al, and after drying a weighed amount was then boiled with conc. HCl for three hours.

Weight of Al_2O_3 used	1·9300 grms.
Weight of Al_2O_3 insoluble	1·3845 ,,

Pionchon (*Comptes Rendus*, cxvii., 328, 330) showed that grey powder was probably Al_6O_7 or $Al_2O_3.3Al_2O_3$. Duboin (*Comptes Rendus*, cxxxii., No. 13) showed that grey powder not a mixture of Al_2O_3 and Al became in mixing Al_2O_3 and 4 Al, and on heating a vigorous action takes place.

Test 3.—A portion of the slag from a Goldschmidt's reduction of Fe_2O_3, after grinding to pass a 40,000-mesh sieve, was boiled with conc. HCl for six hours and nine hours respectively.

Weight of slag used	4·3800 grms.
Weight of insol. matter after six hours .	2·2632 ,,
Weight of insol. matter after nine hours	1·9010 ,,

The filtrate in each case contained Al and Fe.

Conclusion.—It is evident that strongly heated Al_2O_3 is slowly attacked by conc. HCl, and hence in the method of determining constitution of products obtained from Al_4C some of the Al_2O_3 went into solution on boiling with the HCl, as was found by the calculation of results.

The content of Al_4C_3 in the product could have been estimated by determining the volume of CH_4 evolved by the action of water in HCl, but this method was not adopted for two reasons. First, the action of water was extremely slow (1 grm. of the well-powdered substance slowly produced gas for a week and then the action was incomplete); secondly, even on using dilute HCl, the evolution of gas was slow and protracted owing to the protecting layer of Al_2O_3 present; hence the method adopted was the one described.

Analysis of the Gas Evolved by Action of Water and Hydrochloric Acid.

No attempt was made to determine the quantity of gas evolved from known amounts of the solid for the reasons just given, but the gas evolved from different samples

Sample.		Analysis. Free C. Per cent.	Free Al. Per cent.	AlN. Per cent.	Al_4C. Per cent.	Al_2O_3. Per cent.
A. $4Al+3C$:—						
1. Made in open crucible	Top layer	3·3	2·9	22·65	42·09	29·06
	Bottom layer	4·8	2·8	22·83	53·34	16·23
2. Made in closed crucible and heated two hours	Top layer	8·09	1·07	11·84	23·46	55·54
	Bottom layer	7·96	1·40	16·87	36·11	37·66
B. $8Al+3C$: Middle portion, containing blue and yellow crystals		2·29	0·5	40·37	9·12	47·72
C. $4Al+6C$: Lower layer		20·1	0·25	3·67	65·91	11·07

and different portions of the same crucible were carefully examined, with a view to throwing light upon the nature of the carbides present. The samples were placed in small Bohemian flasks (300 cc.), having a side tube in the neck, and connected to a Winchester quart bottle filled with water, which acted as an aspirator gas-holder; the flask was filled with distilled water, and a well-fitting cork inserted into the neck, care being taken to exclude air. The apparatus was then put by and allowed to remain for intervals of time extending from one day to sixteen weeks.

Hempel's technical gas apparatus was used for estimating the constituents of the gas evolved, all the solvents and the containing water in the measuring and pressure burettes being well shaken with the various samples before making observations. Each sample was tested for CO_2, CO, O, and unsaturated hydrocarbons, but in no case was a ny of these gases found. The saturated hydrocarbons and hydrogen were then determined by taking a known volume of the gas, mixing it with a known excess of air, and exploding over water in a Hempel's explosive pipette, measuring diminution in volume absorbing CO_2 produced, and measuring its volume, passing residual gas into alkaline pyrogallic acid, and measuring the volume of O thus absorbed. In order to check this work some half-dozen samples of the gas were likewise analysed in Dr. Bone's apparatus for exact gas analysis over Hg, and the results so obtained did not differ by 1 per cent from the results obtained with Hempel's apparatus. From the diminution in volume after explosion of the volume of CO_2 formed and the volume of O used in explosion, it was deduced that the explosive gas was a mixture of CH_4 and H. In all experiments a gas residue was obtained, which could only be put down as N, and for some time it was a matter of speculation as to the source of this N. Explosions with pure O were carried out, and still the same percentage of residue (N) was obtained. It was, however, noticed that the percentage of N was greater in those samples which had been standing for some time; in fact, those gases which were analysed within twenty-four hours of their starting contained less than 2 per cent, whereas one that had stood three months contained 8 per cent. It was then thought that the N came from the dissolved air in the water used. An active sample of powdered material was therefore treated with water in the apparatus described and the gas analysed at end of known intervals of time in Dr. Bone's apparatus, with the following results :—

At end of twenty hours..	$CH_4 = 43·8$	$H = 52·0$	$N = 4·2$
At end of three days ..	$CH_4 = 43·0$	$H = 51·0$	$N = 6·0$
At end of seven days ..	$CH_4 = 42·5$	$H = 50·3$	$N = 7·2$
At end of fourteen days .	$CH_4 = 42·4$	$H = 50·1$	$N = 7·5$

It will thus be seen that the explanation suggested is the correct one. (That the residual gas was N was confirmed by (*a*) sparking with O over KOH solution, (*b*) spectroscopic investigation).

At first the presence of H in the evolved gases was inexplicable, but when the large amounts of nitride were noticed the explanation was evident. The nitride is slowly decomposed by the water producing NH_3, viz., $AlN+3H_2O = Al(OH)_3+NH_3$. This NH_3 in the presence of water is acted upon by the finely divided Al, similarly to the action of NaOH in Al, with the evolution of H. (About 6 grains of purified Al was placed in distilled water in the generating flask, &c., and at the end of two months not more than 1 cc. of gas had been evolved—this probably came from traces of Fe). To test this hypothesis some of the purified Al powder was placed in the gas-generating apparatus and treated with NH_4OH solution; gas was slowly evolved, and in twelve hours over 200 cc. had been collected, which proved to be nearly pure H (about 2 per cent of N was present from the same cause as before).

Analyses of Gas.

The following analysis is typical of the method used throughout when using Hempel's apparatus :—

Volume of gas taken = 100 cc.
Volume after passing into KOH pipette = 100·0 cc. CO_2 = 0·0 cc.
Volume after passing into P pipette = 100·0 cc. O = 0·0 cc.
Volume after passing into Br pipette and then into KOH pipette = 100·0 cc. Unsaturated hydrocarbon = 0·0 cc.
Volume after passing into acid Cu_2 and Cl_2 pipette = 100·0 cc. CO = 0·0 cc.
Gas passed into P pipette and a sample of it taken for explosion :
Sample taken = 8·3 cc.
Volume sample and air = 99·8 cc.
Volume of air = 91·5 cc.
Volume after explosion = 85·0 cc.
Diminution in volume = 14·8 cc.
Volume after passing into KOH = 78·5 cc.
Volume of CO_2 = 6·5 cc.
Volume after passing into P = 73·8 cc.
Volume of O left = 4·7 cc.
Volume of CH_4 = volume of CO_2 = 6·5 cc.
Diminution due to $CH_4 = 2 \times 6·5 = 13·0$ cc.
Hence volume of $H = \frac{2}{3}(14·8 - 13·0) = \frac{2}{3} \times 1·8 = 1·2$ cc.
Hence volume of $N = 8·3 - (6·5 + 1·2) = 0·6$ cc.
Actual volume of O taken $= \frac{1}{5} \times 91·5 = 18·3$ cc. (approximate).
Volume of O used $= (2 \times 6·5) (+ \frac{1}{2} \times 1·2) = 13 \times 0·6 = 13·6$ cc.
Hence volume of O should = 4·9 cc.
Actual volume found = 4·7 cc.
Composition of gas = 78·3 per cent CH_4, 14·4 per cent H, 7·3 per cent N.

Other samples gave :—

1. Analysed twelve hours after commencement, 78·6 per cent CH_4, 19·1 per cent H, 2·3 per cent N.

2. Analysed three weeks after commencement, 75·0 per cent CH_4, 18·1 per cent H, 6·9 per cent N.

(To be continued).

Royal Institution.—On Tuesday next, May 12, at 3 o'clock, Professor F. T. Trouton begins a course of two lectures at the Royal Institution on (1) "Why Light is believed to be a Vibration," (2) "What it is which Vibrates"; and on Saturday, May 16, Mr. Laurence Binyon commences a course of two lectures on "Japanese Prints." The Friday Evening Discourse on May 15 will be delivered by Dr. H. T. Bulstrode on "The Past and Future of Tuberculosis"; and on May 22, by Professor Dr. J. C. Kapteyn, on "Recent Researches in the Structure of the Universe."

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Annual General Meeting, March 26th, 1908.

Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

Dr. A. McKenzie and Dr. G. T. Morgan were appointed Scrutators, and the ballot was opened for the election of Officers and Council for the ensuing year.

The President announced that communications from Prof. W. J. Pope, Mr. John Allen, and Prof. Adrian J. Brown had been received, stating their unwillingness to accept nomination as Vice-President and as Ordinary Members of Council respectively.

The President presented the Report of the Council, on the progress of the Society during the past twelve months, and the Treasurer gave a statement as to the Society's income and expenditure during the year 1907.

The adoption of the Report of the Council, together with the Balance Sheet and statements of Accounts for the year ended December 31, 1907, was proposed by Prof. A. Liversidge, seconded by Prof. E. Divers, and carried unanimously.

A vote of thanks to the Auditors, which was proposed by Dr. Alexander Scott, seconded by Mr. Otto Hehner, was acknowledged by Dr. H. Forster Morley.

Report of the Council.

As in recent years, the Council have the satisfaction of stating that the prosperity of the Society continues, both the number of papers read and the number of Fellows on the list showing a considerable increase.

On December 31st, 1906, the number of Fellows was 2860. During 1907, 137 Fellows were elected, and 5 reinstated, making a gross total of 3002. The Society has lost 30 Fellows by death; 30 have resigned; 1 election and 1 reinstatement have become void; 1 newly-elected Fellow has withdrawn, and the names of 43 Fellows have been removed from the list for non-payment of Annual Subscriptions.

The total number of Fellows, therefore, at December 31st, 1907, was 2896, showing an increase of 36 over the number for the previous year.

The names of the deceased Fellows, with the dates of their election, are:—A. C. Aitkin (1901), T. Andrews (1870), P. T. Austen (1877), A. Bottle (1873), W. Bowen (1903), E. Chapman (1868), E. D. Chester (1882). J. Clark (1876), George Davey (1893), A. Dupré (1860), J. Gale (1866), Sir D. Gamble, Bart. (1851), S. Hall (1876), L. F. V. Harcourt (1863), B. J. Harrington (1897), J. Ince (1867), F. Keeling (1883), C. O'Sullivan (1876), F. J. M. Page (1871), A. C. Palmer (1906), S. Parfitt (1906), Sir W. H. Perkin (1856), H. D. Perkins (1905), B. C. Polkinghorne (1899), W. Pritchard (1870), R. R. Swann (1905), J. F. Walker (1865), R. Warington (1863), H. A. Wetzel (1883), H. E. Wright (1900).

The number of those Fellows who were elected prior to 1860 has been still further diminished by the death of Sir David Gamble, Bart., who was elected on March 17th, 1851, and Sir William H. Perkin, who was elected on December 15th, 1856.

The number of Honorary and Foreign Members at the close of 1906 was 33. No elections have taken place during 1907, but the Society has to mourn the loss of Prof. Marcellin Berthelot, elected March 1st 1860, deceased March 18th; Prof. Dr. Dmitri Ivanovitsch Mendeleeff, elected February 1st, 1883, deceased February 2nd; Prof. Dr. Nicolai Menschutkin, elected January 20th, 1898, deceased February 5th; and Prof. Henri Moissan, elected January 20th, 1898, deceased February 20th. The number of Honorary and Foreign Members, therefore, at December 31st, 1907, was 29.

During the year 1907, 268 scientific communications have been made to the Society, 203 of which have been published already in the *Transactions*, and abstracts of all have appeared in the *Proceedings*.

The volume of *Transactions* for 1907 contains 2089 pages, of which 2021 are occupied by 205 memoirs, the remaining 68 pages being devoted to the Faraday Lecture, the Obituary Notices, the Report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contains 186 memoirs, which occupy 1890 pages.

The *Journal* for 1907 contains also 4686 abstracts of papers published mainly in foreign journals, which extend to 2100 pages, whilst the abstracts for 1906 numbered 4541, and occupied 1912 pages.

The abstracts for 1907 may be classified as follows:—

	Pages.	No. of Abstracts.
Part I.		
Organic Chemistry	1104	1831
Part II.		
General and Physical Chemistry ..		725
Inorganic Chemistry..		622
Mineralogical Chemistry..		117
Physiological Chemistry		545
Chemistry of Vegetable Physiology and Agriculture		244
Analytical Chemistry		602
	996	2855
Total in Parts I. and II. ..	2100	4686

In the hope of diminishing the confusion which had arisen in the nomenclature of the proteins, consideration of the subject was undertaken by the Publication Committee, in conjunction with representatives of the Physiological Society; the Joint Committee concluded their deliberations early in 1907, and their recommendations appear in the *Proceedings* for that year.

Recognising the importance, from a public standpoint, of the Presidential Address delivered by Prof. Meldola, F.R.S., in March, 1907, the Council have felt it desirable that his remarks on that occasion should attract the attention of a wider circle than is reached by the Society's *Transactions*; accordingly 5000 copies of the Address have been circulated among the members of various public bodies, including both Houses of Parliament, and the Council hope that this unusual step will have the effect of bringing the subject of Prof. Meldola's discourse into suitable prominence.

During the past year, the Society has had to mourn the loss of Sir William Perkin, which took place on July 14th, 1907, just twelve months after the International Celebration which marked the Fiftieth Anniversary of the Foundation of the Coal-tar Colour Industry. This is not the place in which to deal with the splendid achievements of the late Past-President, or the qualities which endeared him to the Fellows, who will remember with melchanoly satisfaction that he lived to participate in the widely-supported public appreciation of the preceding year, and in the subsequent commemoration celebrated in the United States. The marble bust of Sir William Perkin has now been placed in the meeting room, and a large photograph of the portrait painted by Mr. A. S. Cope, A.R.A., is also the property of the Society, having been presented by Sir William a few months before his death.

In view of the losses incurred during recent years through the death of several Honorary and Foreign Members, thereby reducing the number of survivors to 29, the Council recommended for election the following distinguished chemists:—Prof. A. E. J. Gautier, Prof. Albin Haller, Prof. J. W. Hittorf, Prof. J. A. Le Bel, Prof. H. L. Le Chatelier, Prof. T. W. Richards, and Prof. Otto

Wallach. This recommendation was duly ratified by the Society at the meeting on Thursday, February 6th, 1908.

An agreeable feature of the past year has been the Jubilee Celebration of the Société Chimique de France, and on that occasion an Address of congratulation was presented by Sir William Ramsay, F.R.S., on behalf of the Society, which was represented also by Prof. H. E. Armstrong, F.R.S., and Dr. Horace Brown, F.R.S.; a commemorative medal has been received from the French institution and added to the Society's collection. A somewhat similar event took place in September, when the Geological Society celebrated their Centenary, the President being again delegated to offer the felicitations of the Chemical Society. A copy of the recently compiled History of the Geological Society has been since presented to the Library.

Prof. J. Bretland Farmer, F.R.S., accepted the invitation of the Council to deliver a discourse before the Society, and his lecture, entitled, "Some Borderline Problems in Botany," was greatly appreciated by the Fellows.

Late in 1906, Geheimrat Prof. Emil Fischer, F.R.S., an Honorary and Foreign Member since 1892, was nominated Faraday Lecturer, and gave his Address, in German, on October 18th, 1907, in the theatre of the Royal Institution, kindly lent by the managers for the occasion; at the termination of the lecture, entitled "Synthetical Chemistry in its Relation to Biology," the Faraday Medal was presented to Prof. Fischer by the President.

In common with all corporate bodies engaged in scientific pursuits, the Chemical Society has keenly deplored the death of Lord Kelvin, who, although not on the roll of Fellows, has been the guest of the Society on many occasions. At the request of the Council, the President transmitted to Lady Kelvin a resolution of sympathy, and the Society was represented at the funeral ceremony in Westminster Abbey.

Prof. W. Wislicenus, of Tübingen, having initated a memorial to the late Prof. Lothar Meyer, the Treasurer was authorised to contribute from the funds of the Society, and the Council venture to hope that the memorial may be supported by individual Fellows.

The ventilation of the meeting room and council chamber has occupied the attention of the House Committee, who have recommended the installation of electric fans; since their Report was received and adopted by the Council, a Fellow who desires to remain anonymous, has most kindly undertaken to defray the cost of this highly necessary improvement.

In addition to an engraving of Daniell and Faraday, for which the Society is indebted to Prof. Meldola, F.R.S., numerous articles of historical interest and value have come into the possession of the Society in virtue of a bequest by the late Prof. Warington.

The number of books borrowed from the Library during 1907 was 1317, as against 1126 in the previous year. The additions to the Library comprise 138 books, of which 79 were presented, 401 volumes of periodicals (representing 243 journals), and 40 pamphlets, as against 121 books, 385 volumes of periodicals (representing 229 journals), and 32 pamphlets last year.

The experiment of opening the Library during Thursday evenings other than those on which the Society meets has been discontinued, so few Fellows having used the Library on those occasions.

In May, 1907, a special leaflet was issued with the *Journal* indicating the parts required to complete certain sets of periodicals in the Library, in the hope that Fellows happening to possess copies of the desired numbers would present them to the Society. In response to that circular, donations were received from numerous Fellows, and this favourable response has encouraged the Council to hope that further contributions of a similar character may be added to the Library.

As was announced at the last Annual Meeting, the Society received from the Worshipful Company of Goldsmiths a munificent donation of £1000 for the Research Fund. This fund has been still further increased by the handsome sum of £2704 3s. 8d., which was handed over to the Treasurer in July by the Perkin Memorial Fund Committee. These two sums, as now invested, have augmented the annual income of the Research Fund by £126 5s., and will enable the Research Fund Commitee in the present year to recommend the Council to make grants to the amount of £340 to £350. Of this sum, about £34 is more or less especially to be devoted to the encouragement of research in inorganic and metallurgical chemistry, and about £92 for investigations relating to problems connected with the coal-tar and allied industries.

In spite of several items of a somewhat exceptional nature, the Treasurer is glad to be able to report that he has a substantial surplus to carry forward as the result of the year's finance. The income of the Society from all sources for 1907 is £7260 4s. 10d. as against £7121 8s. 11d. in 1906, and the expenditure is £6750 8s. 5d., instead of £6379 15s. 9d., so that, whilst our expenditure has increased by £370 12s. 8d., our income has only grown by £138 15s. 11d. This still leaves a surplus of £509 16s. 5d. on the year's working.

The increase in income may be put down almost entirely to the increase in Annual Subscriptions, for the increase of £100 in the Life Compositions is more than neutralised by the drop of £104 in Admission Fees.

The *Journal* and *Annual Reports* have cost respectively £182 19s. 8d. and £24 8s. 5d. more than last year, but a saving of £23 18s. has been effected on the *Proceedings* and the List of Fellows. The reprinting of certain numbers of the *Proceedings* which were "out of print" has put it within the power of Fellows to complete their sets of *Proceedings*, and the increase in the sale has already more than repaid the cost of the reprints.

A certain amount of redecoration beyond the annual cleaning, the balance of the Dinner account, and the printing and distribution of 5000 copies of last year's Presidential Address are the chief items which have raised the "administrative expenses" so much above those of last year.

In July the Treasurer was able to purchase £1200 North British Railway 3 per cent Debenture Stock; a glance at the balance-sheet will show that the value of the invested capital of the Society was on December 31st, 1907, £18,362 9s. 9d., and that of the Research Fund £10,016 11s. 10d.

A vote of thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year was proposed by Dr. FRANK CLOWES, seconded by Dr. W. E. ADENEY, and unanimously adopted. Prof. J. EMERSON REYNOLDS responded.

The PRESIDENT then delivered his Address entitled "The Electron as an Element."

Prof. RAPHAEL MELDOLA proposed a vote of thanks to the President for his Address and for his services in the Chair during the past year, coupled with the request that he would allow the Address to be printed in the *Transactions* of the Society. Dr. RUDOLPH MESSEL seconded the motion, which was put to the Meeting and carried with acclamation.

The Report of the Scrutators was presented to the President, who declared the following to have been elected as Officers and Council for the ensuing year:—

President—Sir William Ramsay, K.C.B., F.R.S.

Vice-Presidents who have filled the office of President—H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; A. G. Vernon Harcourt, M.A., D.C.L., F.R.S.; Raphael Meldola, F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.A., M.B., F.R.S.; J. Emerson Reynolds, Sc.D., M.D., F.R.S.; Sir Henry E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; T. E. Thorpe, C.B., LL.D., F.R.S.; W. A. Tilden, D.Sc., F.R.S.

Vice-Presidents—J. Campbell Brown, D.Sc., LL.D., J. J. Dobbie, M.A., D.Sc., F.R.S.; F. Stanley Kipping, D.Sc., Ph.D., F.R.S.; Rudolph Messel, Ph.D.; Sir

Alexander Pedler, C.I.E., F.R.S.; W. H. Perkin, Ph.D., F.R.S.

Treasurer—Alexander Scott, M.A., D.Sc., F.R.S.

Secretaries—M. O. Forster. D.Sc., Ph.D., F.R.S.; A.W. Crossley, D.Sc., Ph.D.

Foreign Secretary—Horace T. Brown, LL.D., F.R.S.

Ordinary Members of Council—Julian L. Baker; George T. Beilby, F.R.S.; Alfred C. Chapman; Julius B. Cohen, Ph.D., B.Sc.; J. T. Hewitt, M.A., D.Sc., Ph.D.; W. R. E. Hodgkinson, Ph.D.; H. A. D. Jowett, D.Sc.; H. R. Le Sueur, D.Sc.; F. E. Matthews, Ph.D.; A. G. Perkin, F.R.S.; W. J. Sell, Sc.D., F.R.S.; John Wade, D.Sc.

PHYSICAL SOCIETY.

Ordinary Meeting, April 10th, 1908.

Dr. CHARLES CHREE, F.R.S., President, in the Chair.

Miss E. N. Ladler and Mr. S. D. Chalmers were elected Fellows of the Society.

A paper by Prof. W. H. BRAGG and Mr. MADSEN, entitled "*An Experimental Investigation of the Nature of γ-Rays*," was read by the Secretary. (See CHEMICAL NEWS, xcvii., p. 162).

A paper by Miss D. D. BUTCHER, entitled "*Experiments on Artificial Fulgurites*," was read by Mr. S. SKINNER.

Fulgurites are tubes formed by lightning striking sand or rock and fusing it. The fact that the tubes formed are of two sorts—strong, rocky, thick-walled tubes, and smooth cylindrical tubes with glassy walls—was pointed out by Dr. Fiedler in 1817, and he suggested the possibility that one sort was formed by positive and the other by negative electricity. This idea seemed to be supported by the fact that the cross-section of a thick tube shows a radial structure bearing a marked resemblance to the Lichtenberg figures made by a spark from a positively charged conductor. It was with the view of testing this hypothesis that attempts were made to form fulgurites artificially. The first part of the paper deals with natural fulgurites, and the second with the production of artificial fulgurites. The results of the experiments may be summarised as follows:—

1. The tubes are formed by fusion of the powder which surrounds the column of air in which the spark passes. The length and thickness of the tube depend on the energy of the spark and also on the character of the spark, *i.e.*, whether it is unidirectional or oscillatory. This latter is shown by the fact that the same quantity of energy stored in the Leyden jars does not form a tube when the discharge is abrupt and oscillatory, but forms one if the discharge is rendered less oscillatory by the intervention of a wet string resistance, although a large portion of the energy in the latter arrangement is absorbed in overcoming the resistance of the string.

2. There is no appreciable difference in the two ends of a tube provided that the two electrodes are alike. When one electrode is a point and the other a flat plate, any branching that may occur will be towards the plate whichever electrode is made positive.

In nature, the flat plate would be represented by the moist lower strata of the soil. Therefore we cannot say from the character of the tube whether the lightning discharge was from a positive or negative cloud.

3. The difference between thick and thin tubes is due probably to a difference in the sharpness of the flash and the resulting explosive effect. When the explosive effect is great and the quantity of material melted is small, the result will be a large-bored thin-walled tube. Whether this remains circular or becomes pressed together and distorted, depends merely on whether the fused matter has time to cool before the outward pressure of the blowing has been overcome by the inward pressure on the surrounding sand or not. In Nature, the damp sand or soil probably acts as the damp string in these experiments, and consequently causes many lightning discharges to be unidirectional. In the experimental tubes the outward pressure was so great and the quantity of fused material so small, that the walls were broken through and left as a mere network.

Mr. ALEXANDER RUSSELL congratulated the authoress on her interesting paper. Although he had never found a fulgurite he had noticed several phenomena which seemed connected with their formation. Several years ago during a thunder-shower on the sea, he noticed several flashes striking its surface. Where they struck puffs of steam apparently shot upwards. The appearance was not unlike the splash made by a gannet when diving. It was probably caused by the evaporation of the water in the path of the discharge. Now, a striking peculiarity about fulgurites is that they have a hollow core. The material originally filling it has probably been vapourised. It is therefore highly probable that when a lightning flash strikes sand, a puff of smoke will be shot out from the end of the fulgurite. When testing insulating materials with high voltages, a puff of smoke from the perforation is often the first indication of the breakdown. Electricians frequently notice that when a fuse consisting of a thin wire embedded in sand "blows," a tube of siliceous material is formed. When there is considerable power involved, the tube is raised to a very high temperature and, like the glower of a Nernst lamp, it allows quite a considerable current to pass through it. It would be of interest if the authoress would investigate the conducting power of fulgurites when heated. The difference between thick-walled and thin-walled fulgurites appears to be only one of degree. If we assume that the energy to be got rid of is the same in the two cases, then, when a lightning discharge has a long path to traverse before reaching a good conducting stratum, the fulgurite would in general be thin-walled, but when the path is short it would be thick-walled. It is obvious that a very appreciable amount of energy must have been expended in making some of the fulgurites, parts of which were exhibited.

Dr. C. H. LEES asked if fulgurites, when found, were hollow or filled with sand, &c.

The CHAIRMAN asked if there were any changes in the magnetic properties of a material when it was formed into a fulgurite.

Mr. SKINNER expressed his interest in the remarks of Mr. Russell on the electrical conductivity of fulgurites, and pointed out that if the sand contained salt the fulgurites would probably be conducting. The suggestion that there might be changes in the magnetic properties was interesting and might be tested by experiment.

A paper entitled "*Short Spark Phenomena*" was read by Mr. W. DUDDELL.

The paper deals with two effects which the author has observed in connection with some measurements of the current in the secondary circuit of an induction coil. The apparatus in use consisted of a twelve-inch Newton induction-coil which was supplied from the 200-volt direct-current mains. A large resistance was placed in series with the primary of the coil to limit the current, and the current was interrupted by means of a mercury-jet interrupter. The secondary circuit contained a galvanometer to measure the mean current, and a thermo-ammeter to measure the root mean squared current. When there was no spark-gap in the secondary circuit and the coil was in action, the mean current, as read by the galvanometer, was zero, and the root mean squared current about 3·8 milliampères. If, now, a microscopic spark-gap, say, between two aluminium points, was introduced into the secondary circuit, two curious effects took place. Firstly, the R.M.S. current enormously increased in value, and secondly, a very large deflection was produced on the galvanometer in the direction corresponding to that due to making the primary circuit. The introduction of a spark-

gap one-tenth mm. long caused the R.M.S. current to rise to 38·5 milliampères, and this continued to increase with increasing length of spark-gap until it reached a maximum with a gap about 1·4 mm. The author thinks that this effect is due to very high frequency oscillations set up in the wires connected to the secondary circuit of the coil when a spark-gap is introduced. He has observed the effect with brass, iron, zinc, and aluminium electrodes, but the latter metal is the best to use. The large deflection in the negative direction observed on the galvanometer was investigated by recording the wave-forms of the P.D. and the current by means of an oscillograph. The author showed a series of curves which he had obtained and gave an explanation of the phenomenon. The effects were shown experimentally at the meeting.

Mr. ALEXANDER RUSSELL thanked Mr. Duddell for his valuable paper and for the exceedingly interesting and very successful demonstration of short-spark phenomena. The author's complete analysis of the phenomena he has discovered would be a great help in elucidating the difficult theory of the action of the induction-coil and would throw light on many still unexplained effects. He believed that the change of sign of the direct current component in the secondary circuit of an induction-coil was first discovered by Mr. Duddell, and the Physical Society was to be congratulated on having been the first Society to which this phenomenon was clearly described and demonstrated. He considered that the rise in the value of the effective current when the air-gap was widened was a resonance phenomenon. The capacity *between the electrodes* was in series with the inductance of the secondary, and hence, as the author pointed out, Kelvin oscillatory discharges were continually taking place. The shape of the curve showing the connection between the effective current and the distance between the electrodes was strong evidence in support of this view. The explanation of the direct current component when the electrodes are at considerable distances apart, may be made by remembering that the wave pulses of E.M.F. round the secondary at "make" and "break" are of very different shapes although their integral values are the same. The maximum value of the induced E.M.F. at break is much greater and the consequent rush of electricity is more "impulsive" than at make. Hence, when the electrodes are sufficiently far apart the air-gap is only broken down by the break E.M.F., and so we get a unidirectional pulsating current of triangular shape. When the electrodes are closer together we get an alternating current, the shape of the positive and negative waves being quite different owing to the differently shaped waves of E.M.F. at make and break. When they are very close together, the author's oscillograms show that we get a pulsating unidirectional current in the direction due to the "make" E.M.F. The reason for this strange phenomenon is by no means obvious.

Mr. S. SKINNER expressed his interest in the paper, and referred to the experiments on the electrolysis of steam carried out by J. J. Thomson by a modification of Perrot's method. He found that with short sparks the hydrogen appeared at the positive electrode instead of at the negative as in ordinary electrolysis. Perhaps this phenomenon was due to the same causes as the effects shown by the author.

Dr. R. S. WILLOWS asked if the maximum current obtained was connected in any way with the minimum sparkling voltage.

Prof. CASSIE pointed out that the minimum sparking voltage occurred at distances very much less than those used in Mr. Duddell's experiments.

Mr. C. C. PATTERSON asked if the author had tried experiments with spark-gaps of different capacities.

Mr. A. CAMPBELL asked if it was possible that the rectifying action of the spark-gap might be similar to that of an ordinary aluminium electrolytic rectifier.

Mr. DUDDELL said he did not think the effect was in any way connected with the minimum sparking voltage. He had tried varying the materials of the electrodes and using electrodes of various capacities, and the effect was the same.

ROYAL INSTITUTION.

Annual Meeting, May 1st, 1908.

Sir JAMES CRICHTON-BROWNE, Treasurer and Vice-President, in the Chair.

THE Annual Report of the Committee of Visitors for the year 1907, testifying to the continued prosperity and efficient management of the Institution, was read and adopted, and the Report on the Davy-Faraday Research Laboratory of the Royal Institution, which accompanied it, was also read.

Forty-one new Members were elected in 1907. Sixty-three Lectures and nineteen evening Discourses were delivered in 1907. The books and pamphlets presented amounted to about 203 volumes, making with 693 volumes (including periodicals bound) purchased by the Managers, a total of 896 volumes added to the Library in the year.

Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committee of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year.

The following gentlemen were unanimously elected as Officers for the ensuing year :—

President—The Duke of Northumberland.

Treasurer—Sir James Crichton-Browne.

Secretary—Sir William Crookes.

Managers—Sir Thomas Barlow, Bart., Sir George Darwin, The Rt. Hon. The Earl of Halsbury, W. A. B. Burdett-Coutts, Charles Hawksley, Dr. Donald William Charles Hood, Dr. Rudolph Messel, Henry Francis Makins, George Matthey, Dr. Ludwig Mond, The Rt. Hon. Sir John Fletcher Moulton, Alexander Siemens, The Rt. Hon. Sir James Stirling, The Rt. Hon. The Earl of Rosse, and Sir William H. White.

Visitors—Arthur N. Butt, Dugald Clerk, Charles A. Ballance, John B. Broun Morison, Edward Dent, John Cameron Graham, Dr. James Dundas Grant, Charles Edward Groves, Sir Henry Harben, Major E. H. Hills, John List, Robert Mond, Francis Lys Smith, James Swinburne, and Lieut.-Colonel Sir Frederick Nathan.

CORRESPONDENCE.

THE PERIODIC LAW.

To the Editor of the Chemical News.

SIR,—I have noticed recently the difficulty experienced by more than one writer in fitting new elements into the tables which represent existing classifications. The obvious effort in every table is to conform to the Period 8, and the difficulty in doing so is well illustrated in Group VIII. of the table which is due to the genius of Mendeleeff. There does not appear to me to be any very weighty reason why the tables should be limited to eight groups, and if there is no such reason then the effort to make all elements fit into eight neatly ruled-off compartments seems to be misplaced.

It is not, however, my object to dwell on well-known difficulties, but to point out a direction for work that may lead round them.

1. Inorganic evolution, as developed, for instance, by Sir Norman Lockyer in his well-known work of that name, will, I think, be admitted as a possibility by most people. If it is so admitted, we must consider the heavier atoms as being built up either of the lighter, or of groups of corpuscles still more elemen-

tary than the lightest atoms known. In either case there should then be a simple numerical relation extending throughout the whole atomic series. We should then expect to be able to tabulate the elements in accordance with the form of the series which shows this relation.

2. Periodicity is unquestionable, and the reason of it should be traceable to the recurrence of particular intra-atomic grouping, or of the same group which, whilst preserving its own individuality, might be attached to a larger group. In either case, each recurrence should be a well-marked feature in the series, and should be plainly shown in the scheme of tabulation.

3. Considered as a series, perhaps the most remarkable correlative attribute of the elements is their specific gravity. The specific gravity atomic weight curve must be a graphic expression of the internal peculiarities which determine atomic individuality, and should therefore not be lost sight of in formulating a scheme of tabulation.

If we allow that there is any weight in arguments Nos. 1, 2, and 3, then our tabulation should primarily take the form of a definite series to satisfy No. 1. To satisfy No. 2 the numbers which represent the elements should be broken up into parts, in such a way that the recurrence of parts shall have the same periodicity as elemental properties. This is plain when we remember that in any table, no matter what its properties, an element is represented solely as a number. To satisfy No. 3 the form of the series must show a plain relation to the specific gravity curve.

If now we consider the peculiar position of the members of Group VIII. in Mendeleeff's table with respect to the vacant spaces in the zero group, and also consider the position occupied by the elements of the latter group in the specific gravity curve, I think we can form a very good idea of the general form of the atomic series.

We may write the following series as representing the general form that will satisfy requirement No. 1 :—

TABLE I.

							3	4
							7	8
				11	12	15	16	
	19	20	23	24	27	28	31	32
&c.	—	—	55	56	59	60	63	64
				&c.	—	—	127	128
					&c.	—	—	256

Wherein the number in the last column is severally added to itself and all previous smaller numbers to give the next step in the series. This arrangement does not, however, satisfy Nos. 2 and 3. A little analysis of the above figures will enable us to make the disposition shown in Table II., taking for the purpose of illustration the zero group as a basis. It may be mentioned in passing that the halogen group or the lithium group gives more easily defensible results, but require at the same time more explanation. To emphasise the relation I show the parts that give us a close approximation to the even-number elements, omitting the others.

It will be noticed that this arrangement outlines a definite series of numbers that closely approximate the atomic weights of the elements. The steps in the series follow exactly the undulations in the specific gravity curve, but the periodic recurrence of parts with properties is not exact, fractions are not accounted for, and there are other minor irregularities and divergences which require explanation.

If it is conceivable that the atoms are made up of definite groups, it appears to be also reasonable, and I think necessary, to suppose that free corpuscles may be attached to the atoms or sub-groups. Sir William Ramsay has pointed out to me that these must affect the weight, and

TABLE II.

| PRIMARY PARTS. | SECONDARY PARTS. | | | | | | | |

might possibly account for fractions and other divergences from a main fundamental series, if one exists.

I will not go into this question here as it requires a lengthy analysis, and also as the introduction of a third small part will not affect the general form of tabulation which is advocated.

I think that the figures already given will show that, whilst the fitting of the elements to existing classifications may be productive of very interesting and useful results, the converse operation—fitting the classification to the elements—is likely to be quite as fruitful, and for many reasons would appear to be more logical.—I am, &c.,

W. DENHAM VERSCHOYLE.

NOTICES OF BOOKS.

The Chemistry of the Diazo-chmpounds. By JOHN CANNELL CAIN, D.Sc. (Manchester and Tübingen). London: Edward Arnold. 1908.

IN this book a complete account is given of our present knowledge of the diazo-compounds and their most important derivatives. In the first part the preparation and reactions of the compounds are described, the historical order of discovery being adopted, while the theory of their constitution is reserved for the later part of the book. Here, again, the order is historical, and a full discussion of the controversy between Hantzsch and Bamberger on the structure of the diazo-compounds is included. Students interested in organic chemistry will be glad to receive this particularly clear analysis of a question upon which it is difficult to decide from the study of the original papers owing to the great mass of detail with which they are necessarily encumbered. In an appendix the author suggests a new theory relating to the constitution of the diazo-compounds which he thinks may possess a quinonoid structure. This theory undoubtedly throws light upon some of the reactions of the compounds, which are difficult to explain otherwise; for example, the readiness with which the whole of the diazo-nitrogen is eliminated, whereas in all other cases singly-linked nitrogen appears to be bound firmly to the benzene nucleus. As far as can be seen from the outline no tenable objection can be advanced against the author's theory, and thus the book, both as a compilation and as an original contribution to organic chemistry, constitutes a valuable monograph.

La Psychologie Inconnue. Introduction et Contribution à l'Etude Expérimentale des Sciences Psychiques. ("Unknown Psychology. An Introduction and Contribution to the Experimental Study of Psychic Science"). By EMILE BOIRAC. Paris: Félix Alcan. 1908.

THIS work contains a collection of the articles dealing with experimental psychology which the author has written for various periodicals. The papers are welded together into a continuous whole, and thus the book constitutes a general survey of the whole of this branch of science. The author divides the subject under three heads:—Hypnotic phenomena, magnetic phenomena, and psychic phenomena. He endeavours to examine into the evidence for the various experiences which have been reported, and to refute the main arguments of his adversaries. The views of the schools of Paris and Nancy are specially discussed. The anthor states his opinions very clearly, and attacks the subject in a thoroughly scientific spirit, proceeding from the investigation of the simplest phenomena to the study of those which are more complicated, and thus laying a firm foundation for the development of the science upon well attested lines. Magnetism is specially considered, the author believing that it is accountable for definite and characteristic phenomena.

Quarterly Journal of the Institute of Commercial Research in the Tropics. Vol. III., No. 6. Liverpool: The Offices of the Institute. London: Williams and Norgate. 1908.

IT is impossible to over-estimate the value of the work which is being done by the Liverpool Institute of Commercial Research in the Tropics, and each number of the Quarterly Reports issued bears witness to the zeal and activity of the scientific staff. The most important papers in this volume are those by D. Spence, Ph.D., on the distribution of the protein in Para-rubber and on the analysis of the latex from *Ficus Vogelii*. In addition, the possibilities of the oil palm in cultivation is discussed by Dr. Drabble in an article in which practical suggestions are made relating to the most suitable varieties for planting, and the use of white mangrove for tanning is another subject which is of considerable commercial importance. Every one of the seventeen papers which are contained in the journal is full of valuable material for all who are interested in the development of the tropics, and a most encouraging account is given of the Liverpool Tropical Products Exhibition which was held last autumn.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 10. March 9, 1908.

Neutral Carbonates of Alkalis and Alkaline Earths.—M. de Forcrand.—The author has investigated the decomposition by heat of the neutral carbonates of the alkaline earths and alkalis, and has compared the results with the corresponding thermo-chemical data. As a general result he has found that the temperature of dissociation of the carbonates of calcium, lithium, strontium, and barium is always lower than that deduced from thermo-chemical data, the difference increasing from calcium to barium. Probably the heat of formation of calcium carbonate, for instance, is lower at a high than at the ordinary temperature.

Combustion without a Flame, and Ignition of Gases at the End of a Strip of Metal.—Jean Meunier.—The author has studied the combustion of gases in a spirit lamp in which the flame is spread by a metallic disc which serves to mix the spirit and air, and a rod of metal runs up the central cylinder. When the perforated disc gets red-hot the flame dies down. The flameless combustion of gases and vapours is localised at the surface of the disc, and the combustible gases are collected round the disc. When a lighted match is brought near the rod of metal the flame at its extremity is attracted by the flame of the match. This seems to show that gases have a certain cohesion, and will rise along a rod of metal without mixing with neighbouring gases, as if they were protected by a solid envelope.

MEETINGS FOR THE WEEK

TUESDAY, 12th.—Royal Institution, 3. "Why Light is believed to be a Vibration," by Prof. F. T. Trouton, F.R.S., &c.

WEDNESDAY, 13th.—Royal Society of Arts, 8. "The Underground Water Supplies of the Thames Basin," by Clayton Beadle.

THURSDAY, 14th.—Royal Institution, 3. (The Tyndall Lectures). "Mendelian Heredity," by William Bateson, F.R.S., &c.

FRIDAY, 15th.—Royal Institution, 9. "The Past and Future of Tuberculosis," by H. T. Bulstrode, M.D., D.P.H.

SATURDAY, 16th.—Royal Institution, 3. "Japanese Prints," by Laurence Binyon.

THE CHEMICAL NEWS.

Vol. XCVII., No. 2529.

ON THE ATOMIC WEIGHT OF RADIUM.*

By T. E. THORPE, C.B., LL.D., F.R.S.

Although there has been a considerable amount of discussion, based upon spectroscopic considerations and on its supposed mode of genesis, respecting the place of radium in the system of the elements, and inferentially, therefore, concerning its atomic weight, we are indebted for the only direct experimental determinations of this value hitherto made known to the discoverer of the element, Mdme. Curie. Her first observations, published in 1902, were made on about 90 mgrms. of the chloride, and furnished the value 225 as the mean of three fairly concordant experiments (*Ann. de Chim. et de Phys.*, 1903, xxx.).

In the autumn of last year Mdme. Curie communicated to the French Academy the results of a second series of estimations. These were made upon much larger quantities of the carefully purified chloride (about 4 decigrms.), and afforded the value 226·2 as the mean of three closely concordant determinations (Ag=107·8, Cl=35·4) (*Comptes Rendus*, 1907, cxlv., 422; "La Radium," October, 1907).

In 1906, at the instance of Sir William Huggins, then President of the Society, and by the aid of the kind interest shown by H.R.H. the Prince of Wales, the Austrian Government placed about 500 kilogrms. of pitchblende residues from the mine at Joachimsthal at the disposal of the Royal Society. These residues were sent to be worked up by M. Armet de Lisle at his factory at Nogent-sur-Marne, by the method employed by him in the case of the material which served M. and Mdme. Curie for their researches. The funds for both these purposes were defrayed from a grant made by the Goldsmiths' Company to the Royal Society in 1904 for the purpose of the investigation of radium.

The residues, as received by M. Armet de Lisle, were stated to have a radio-activity of about two and a-half times that of uranium.

The process of extraction employed by M. Armet de Lisle resulted in the production of about 413 grms. of practically anhydrous barium chloride, containing radium chloride suffic ent to give the salt a radio-activity 560 times that of uranium.

This salt was received by the Royal Society in the autumn of 1906, and was handed to me in January, 1907, with the request that I would extract the radium chloride from it, and undertake, if possible, a re-determination of the atomic weight of the element. This in view of the discussion, already referred to, which was then taking place, as to the relation of radium to certain other elements, seemed at the time the most profitable use to which the radium salt, when extracted, could be put. When received by me the barium-radium chloride was distinctly cream-coloured, and the bottle in which it was contained was coloured violet.

The method of extraction was substantially the same as that originally adopted by Mdme. Curie, and described in her thesis (*loc. cit.*), namely, systematic fractional crystallation, first from water and then from increasingly strong hydrochloric acid, until finally the acid used was the strongest that could be obtained by distillation. All the solvents employed were carefully purified, the acid being distilled in a platinum retort, and preserved in a platinum bottle. The crystallisations were made first in porcelain, subsequently in Jena glass, and finally, as the radio-active matter became more and more concentrated, in vessels of fused rock-crystal. Every precaution was taken to guard against loss and accidents, and to ensure the recovery of the radium should such occur. It is satisfactory to be able to state that the whole scheme of extraction, involving some 9400 re-crystallisations, was carried through without a mishap.

I have to thank Mdme. Curie for her courtesy in affording me information concerning certain details of her method of isolating the radium salt. At the outset of our exchange of letters she informed me, of what at the time I was unaware, that she was then actually engaged on the same problem, and she has since, as already stated, published the results of her determinations. She was good enough, however, to express the hope that I would continue the work which I had been requested to undertake, in view of the desirability of gaining all possible knowledge as to the true atomic weight of the element.

During the autumn of 1907, whilst still engaged in the isolation of the radium chloride from the material furnished by M. Armet de Lisle, I received a further small supply of radium from the Royal Society. It was bought in Cambridge, and was of German origin, and had been purchased through the instrumentality of Prof. Liveing. It purported to be radium bromide, but on removing it from the metallic capsule in which it had been stored since 1903, it was found to be wholly insoluble in water. On treatment with pure dilute hydrobromic acid it readily passed into solution. The salt obtained by evaporation was sent to Prof. Rutherford, who had kindly undertaken to make any measurements of radio-activity which I needed. He estimated the amount of radium present as equivalent to 33 mgrms. of radium bromide.

This salt was eventually converted into chloride, and was purified by repeated crystallisation from strong hydrochloric acid.

Traces of lead cling persistently to the radium chloride thus separated by means of hydrochloric acid. Mdme. Curie was so kind as to draw my special attention to this fact, and accordingly care was taken to remove this metal. When practically the whole of the radio-active matter had been concentrated into a few grms. of the material, this was dissolved in water acidulated with hydrochloric acid, and treated with sulphuretted hydrogen out of contact with air. A small precipitate of lead sulphide was formed. The liquid was further treated with sulphuretted hydrogen, the lead sulphide removed by filtration, the filtrate evaporated to dryness, the residue treated with strong hydrochloric acid, and the process of fractionation resumed. That the precipitate was lead sulphide was confirmed by its conversion into the yellow iodide.

Determination of Atomic Weight.

This was effected by ascertaining the amount of silver chloride yielded by a weighed quantity of the anhydrous radium chloride—the principle of the method already employed by Mdme. Curie.

Since it was very improbable that the amount of the radium salt at my disposal would amount to as much as a decigrm., it was absolutely necessary so to arrange the process of carrying out the estimations as to minimise, to the greatest possible extent, the errors due to manipulation. Accordingly a method was devised whereby the whole of the operations of drying and weighing the radium chloride, precipitating, washing, drying, and weighing the silver chloride, might be performed in one and the same vessel, thus obviating the necessity of transferring the silver salt, and of separating it by any of the ordinary processes of filtration.

The vessel in which these operations were made consisted of a thin glass tube with a conical base furnished with a hollow well-ground stopper. It had a capacity of about 15 cc., and was as light as was consistent with the requisite strength, and could be suspended from the balance-arm by fine platinum wire. In all the weighings a precisely similar bottle of almost identical weight and

* Bakerian Lecture for 1907. Delivered before the Royal Society, June 20, 1907.

capacity, suspended in like manner, was employed as a tare. The weighings were made on a very sensitive assay balance, with 4-inch arms, carrying a maximum load of 12 grms., and provided with light stirrup pans. I am indebted to Mr. Oertling for the loan of it. It was a beautifully finished instrument of great delicacy, and remarkably constant in its indications (Fig. 1).

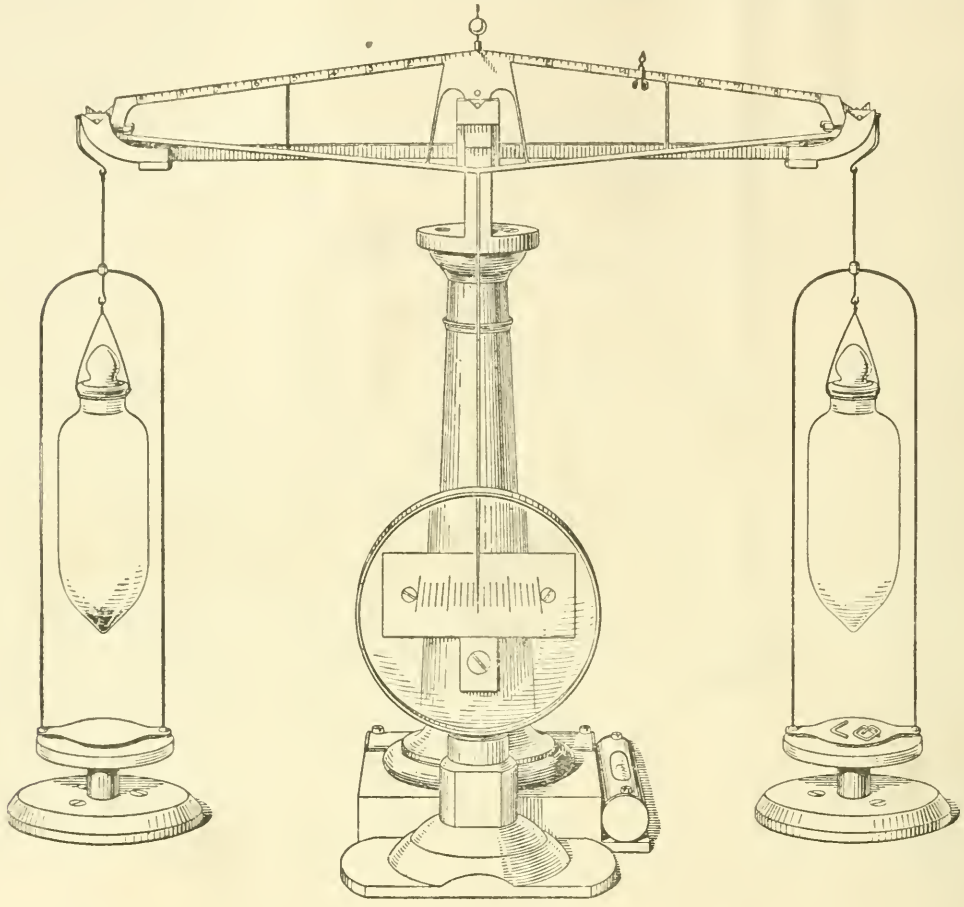


Fig. 1.

The weights were also of Oertling's make, and were compared before use with a standard set belonging to the Government Laboratory.

A room was specially set apart and arranged for the determinative work. It was a small apartment on one of the upper floors of the Government Laboratory, and had a wooden block floor arranged "herring bone" fashion. The walls of the building were subject to a very slight tremor, due to a small steam-engine in the basement. The balance table therefore was not bolted to the walls, as is the usual practice, but was placed directly on the floor, which, by reason of its mode of construction, was less susceptible to tremor than the walls. The legs of the table stood on packets of filter-paper, as did also the levelling screws of the balance case. Under these conditions the balance was found to be quite free from tremor, and the levels remained absolutely constant throughout the entire course of the work.

The weighings were made by the method of vibrations, the zero-point being determined before and after each determination.

The course of the operations was as follows:—The small glass vessel and its tare were first heated to about 150° in an air-bath for an hour, and allowed to stand over-night in a desiccator containing phosphoric oxide. They were then weighed one against the other in the manner described. The chloride, previously dried at 140° to 150°, was next transferred by means of a platinum spatula from the rock-crystal basin in which it was contained, to the glass vessel, and this and its tare were again heated to 150° for about an hour in the air-bath, and after standing over-night in the desiccator containing phosphoric oxide, were again weighed. The chloride was then dissolved in 2 cc. of distilled water, the solution acidulated with two drops of dilute nitric acid (1 : 4), warmed, and mixed with a slight excess of silver nitrate solution of known strength added drop by drop, with constant shaking, from a narrow burette capable of being read to 1/50 cc. When clear, the liquid was again tested with the silver nitrate solution in order to ascertain that the precipitation was complete, and after standing for about eighteen hours in a warm place when the silver chloride had wholly subsided into the bottom of the conical portion of the vessel, the clear supernatant solution was drawn off by means of a capillary glass tube.

This was conveniently effected in the manner illustrated by Fig. 2. The vessel (*a*) containing the silver chloride was placed on a small elevating table (*b*), the height of which could be adjusted by means of the rack and pinion arrangement seen at (*c*), so that the end of the drawn-out capillary syphon (*d*), made of thermometer tubing, could be brought to within a mm. or two of the deposit of silver chloride. By gentle aspiration at (*e*) the action of the syphon was started, and by far the greater quantity of the

clear liquid could be drawn over into the flask (*f*) without the slightest risk of disturbing the precipitate.

The table was then lowered, and the end of the syphon as well as the internal sides of the vessel washed by a fine stream of hot distilled water. After clarification, the wash-water, which was about 4 or 5 cc. in bulk, was drawn over as before, and the process repeated. After each addition of hot water the vessel containing the silver chloride was well shaken, and the precipitate broken up by means of a fine platinum wire, so as to bring the washing water in thorough contact with it. As is well known, silver chloride which has become granular by standing shows little or no tendency to occlude soluble matter, and is readily washed. Both the end of the syphon and the platinum wire were always washed by a stream of hot water, and were carefully examined by a lens, but in no case was any silver chloride found to have become attached. The liquid drawn over was invariably perfectly clear.

Assuming that we have 100 mgrms. of soluble matter in the 4 cc. of the clear supernatant liquid, and that we draw over 3·5 cc. at each successive operation as above described, it is readily calculable that the amount of matter in solution, even after the third operation, is probably too small to be appreciated by the balance.

The following table shows how rapidly the soluble matter is removed by systematic washing in the manner described :—

	Mgrms.
Original solution contains	100
After first decantation, residual liquid ..	12·5
,, first washing ,, ,, ..	1·56
,, second ,, ,, ,, ..	0·19
,, third ,, ,, ,, ..	0·02
,, fourth ,, ,, ,, ..	0·003
,, fifth ,, ,, ,, ..	0·0004

As the precipitated silver haloid was always thus washed six times in succession, it may be assumed that it was practically freed from all soluble matter.

Care was of course taken to protect the silver chloride from the action of light, and to the extent that was practicable all the operations were carried out in a photographic dark room which adjoined the small laboratory set aside for the work. No matter what precautions were taken to exclude ordinary white light, the silver chloride invariably became violet in contact with radium solutions.

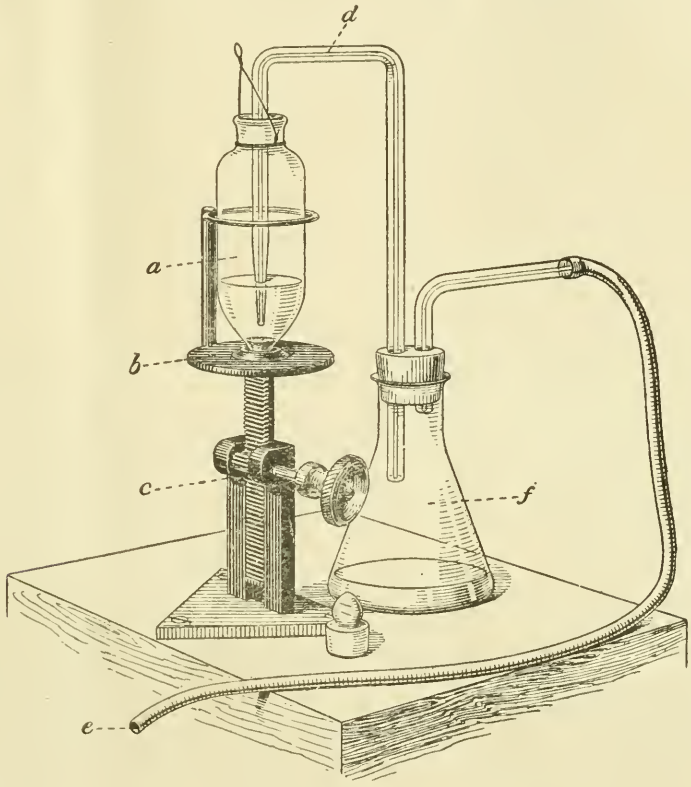


Fig. 2.

The washed silver chloride was first dried at 100°, and then heated in the air-bath to 160° for about a couple of hours, and, after standing in the desiccator over phosphoric oxide for about eighteen hours, weighed in the manner described.

In order to test the practicability of the method and to acquire experience of its working, as well as to gain some idea of its accuracy before actually making use of it in the case of the radium salt, a series of determinations of atomic weight was made with barium chloride, purified by systematic re-crystallisation from water, according to the method already indicated, the same apparatus, reagents, and solutions being employed as were to be used subsequently in the radium determinations.

The results were as follows :—

Ag = 107·93. Cl = 35·45.

Barium chloride. Mgrms.	Silver chloride. Mgrms.	Atomic weight Ba.
114·7	157·8	137·5
172·1	236·8	137·5
57·1	78·8	136·9
62·6	86·1	137·6
68·1	93·7	137·5

As the corrections for displaced air for the silver chloride and for the barium chloride only amount to 0·00007 and 0·0002 per grm. respectively, they are of course wholly negligible in the case of quantities so small as were actually employed. The value for barium adopted by the International Committee on Atomic Weights, 1907-8, is 137·4

These determinations were made on independent amounts of material. As the quantity of radium salt I could hope to obtain would almost certainly not suffice to enable me to make similar independent determinations, it was desirable to prove that the element, which would exist in the solution in association with nitric acid after the precipitation of the chlorine as silver chloride, could be recovered and re-converted into chloride, and that the operations necessary to effect this would not influence the value of the atomic weight in a subsequent determination.

The first step was to remove the excess of silver in solution. This might be effected by means of hydrochloric acid. A difficulty at once presented itself. Silver chloride is not wholly insoluble in solutions of hydrochloric acid and of the chlorides of the alkaline earths, and presumably, therefore, in solutions of radium chloride. It was consequently necessary so to apportion the hydrochloric acid as to effect the precipitation of the silver without leaving any considerable excess of hydrochloric acid in solution. As the amount of the silver originally used, as well as that in the weighed silver chloride, were known, it was easy to calculate the amount remaining in solution, and so determine the quantity of hydrochloric acid required to precipitate it. This amount of hydrochloric acid, contained in a dilute solution of known strength, was then cautiously added, drop by drop, with constant shaking, and when the liquid was sufficiently clear it was tested, to ascertain that the precipitation was complete, by the addition of a single drop of the hydrochloric acid solution.

After standing until perfectly clear, the supernatant liquid was drawn off by the capillary syphon, the silver chloride thoroughly washed in the manner already described, and the solution transferred to a silica basin, and evaporated to dryness over a water-bath heated with an alcohol lamp to avoid any possible action of the oxides of sulphur produced by the combustion of London coal-gas.

The dried residue was then repeatedly evaporated with small quantities of pure hydrochloric acid, and so reconverted into the chloride.

Two determinations of the atomic weight of barium, made in the manner described on barium chloride thus recovered, gave the following results :—

Barium chloride.	Silver chloride.	Atomic weight Ba.
Mgrms.	Mgrms.	
139·5	191·4	138·1
78·8	108·3	137·7

In the hope that I might be able to employ the bromide of radium in the determination of the atomic weight of this element, I also made a similar preliminary series of determinations of the atomic weight of barium by means of barium bromide prepared from the pure chloride, and repeatedly re-crystallised from alcohol.

The results were as follows :—

Ag = 107·93. Br = 79·96.

Barium bromide.	Silver bromide.	Atomic weight Ba.
Mgrms.	Mgrms.	
89·9	113·6	137·5
96·0	121·4	137·3
111·0	140·3	137·4

Two determinations were made on the recovered barium bromide, with the following results :—

Barium bromide.	Silver bromide.	Atomic weight Ba.
Mgrms.	Mgrms.	
91·0	114·9	137·7
80·8	102·1	137·5

It will be seen from these numbers that a very close approximation to the true atomic weight of barium can be obtained by the method described, the maximum error being about half a unit, or less than 0·5 per cent. Considering that the atomic weight of radium is probably nearly double that of barium, the same fortuitous errors would affect its value to about a unit.

There is, however, one circumstance which, whilst not without influence in raising the value of barium, when determined on the recovered chloride, hardly affects the value of radium. In the case of radium, the effect of any minute quantity of retained silver haloid in the recovered salt, provided it is weighed with the precipitated silver chloride, is practically negligible, since radium chloride gives approximately its own weight of silver chloride.

As the work of isolating and purifying the radium chloride proceeded, determinations of the amount of chlorine were made as described from time to time, and as soon as approximately constant values were obtained it was assumed that any barium or other impurity present was too small in amount to affect the results when regard was had to the unavoidable experimental errors. The resulting chloride was then repeatedly and carefully recrystallised from pure strong hydrochloric acid, the "tails," which were comparatively rich in radium, being specially set apart.

The purified salt finally extracted from the material supplied by M. Armet de Lisle weighed, when anhydrous, 64 mgrms.

I regard this salt as substantially radium chloride. I am not, however, in a position to say that it was absolutely free from barium. At the same time, I have reason to believe that the amount still present was probably too small to materially influence the result, considering the limited quantity of the salt I had to work with, and the consequent relatively large experimental errors.

With the aid of Sir William Huggins, who kindly made the spectroscopic trials for me, I was able to carry out Mdme. Curie's test of comparing the relative intensity of the lines of barium and radium in the spark spectrum of the separated radium chloride. Mdme. Curie compared the relative strengths of lines 4554·2 of Ba and 4533·3 of Rd. Although these have the advantage of being close together, they are of dissimilar intensity. Sir William Huggins advised that a more stringent test would be to take the line 5536·2 of Ba of intensity 10, and compare it with the Rd lines 5813·8 and 5560·8, which are also of intensity 10. On actually making the trials, which were repeated several times, the green Ba line 5536·2, although visible, was seen to be relatively very feeble—less intense, indeed, than that afforded by the most dilute solution of barium chloride that we were able to employ.

With this material, therefore, I attempted to make the determination of atomic weight. Accordingly, the greater portion was transferred to the vessel already described, and the amount of chlorine in the anhydrous salt determined with all possible care. The result was :—

Radium chloride.	Silver chloride.	Atomic weight Rd.
Mgrms.	Mgrms.	
62·7	60·4	226·8

The radium was recovered from the solution, re-converted into chloride, added to what remained of the original quantity, and the amount of chlorine again determined in the anhydrous salt. The second result was :—

Radium chloride.	Silver chloride.	Atomic weight Rd.
Mgrms.	Mgrms.	
63·9	61·8	225·7

The purified chloride obtained from the Cambridge material amounted to 24 mgrms. A chlorine determination on a portion gave a number exceeding 230 for the atomic weight. No more importance can be attached to this value, considering the very small amount employed, than as showing that the salt was of the same order of purity as that obtained from the French material.

It was accordingly added to the main bulk, and the whole was repeatedly crystallised from strong hydrochloric

acid, about 6 mgrms. being thus removed in the mother-liquors. The resulting chloride, after being dried at 150°, was again analysed with the following results :—

Radium chloride.	Silver chloride.	Atomic weight Rd.
Mgrm.	Mgrm.	
78·4	75·3	227·7

The mean value is 226·7, or, to the nearest unit, 227. This, it will be observed, is in very close accord with Mdme. Curie's latest number.

I think, therefore, it is reasonably well established that the atomic weight of radium is now known to within a unit which, considering the relatively high number, is, under the present circumstances, as fair a degree of exactitude as could be anticipated.

There are, however, one or two facts connected with the behaviour of radium chloride which, as they may possibly affect the determination of its atomic weight, may here be mentioned. If a quantity of the salt be kept in perfectly dry air, it will be noticed that it very slowly increases in weight. The increase is very small, but it is plainly perceptible on a sufficiently delicate balance, and in the course of three or four days may amount to 0·3 per cent. On opening the vessel a marked smell of ozone is perceived, and on aspirating the air from above the chloride by means of a capillary tube passing into a freshly-prepared solution of potassium iodide and starch, iodine is found to be liberated, as seen from its action on the starch. Moreover, on dissolving radium chloride which has stood for some time in contact with the air in warm water, and acidulating the solution with dilute nitric acid, a smell recalling that of hypochlorous acid is perceived. The observed increase in weight may be due, therefore, to a portion of the air in the vessel becoming ozonised, or to a slight oxidation of the chloride, or to both these causes combined. Their joint effect would tend to increase the atomic weight of radium.

Another remarkable circumstance connected with radium chloride is its action on colourless rock-crystal, which is gradually turned a deep purplish black. Berthelot has already drawn attention to the action of radium on quartz. The silica vessels which I employed in connection with the foregoing work were thus strongly coloured in the course of a few months. Moreover, these vessels, as well as those of porcelain and glass, are slightly attacked by radium chloride, with the formation, apparently, of insoluble silicates. A similar observation has been made by Mdme. Curie. It occasionally happened that a sample of radium chloride, after standing for some considerable time in contact with glass, gave a faintly turbid solution, although when the salt was newly crystallised from hydrochloric acid its aqueous solution was perfectly clear.

I had hoped, as stated, to have obtained an additional series of values for the atomic weight of radium by the analysis of the bromide. As already mentioned, I reconverted the Cambridge material into this salt; but my experience with it leads me to infer that it is not sufficiently stable to afford trustworthy values for the atomic weight of the element. It appears to lose bromine, and eventually becomes insoluble in water. I hope to be able to study this change more minutely, as well as to throw some additional light on the action of radium salts on glass.

In conclusion, I desire to acknowledge my indebtedness to my assistant, Mr. Arthur G. Francis, B.Sc., for the assiduity, conscientiousness, and skill with which he has carried through what has proved to be the most irksome and tedious part of the work, namely, the isolation and purification of the radium chloride.

I am also indebted to Prof. Rutherford for the measurements of radio-activity which he made for me in the course of the fractionation of my material.

Royal Institution.—On Thursday next, May 21, at 3 o'clock, Dr. Alexander Scott will deliver the first of a course of three lectures at the Royal Institution on "The Chemistry of Photography."

THE INTERACTION OF ALUMINIUM POWDER AND CARBON.*

By FRANK E. WESTON, B.Sc., and H. RUSSELL ELLIS, B.Sc.

(Concluded from p. 222).

Series II.—*Aluminium Powder and Charcoal.*

The sugar carbon was made from white lump sugar by heating small portions at a time in a cylindrical tin and finally heating in the muffle to 1000°—1100° C. It was well crushed on cooling, powdered, and sifted through 40,000-mesh sieve; it was a bright, shiny powder, hard and difficult to crush, and it did not seem at all porous. The percentage of ash was none.

Mixtures 4 Al + 3 C.—The interaction was tried in four ways.

Method 1.—Mixture was placed in a Hessian crucible and embedded in sand, so that the crucible could be covered with a beaker and air excluded. The action was started with a fuse and spread slowly over the top, but on covering over with a beaker it ceased. This was found to be the case on repeating several times. The reaction proceeded when left uncovered. It thus appears that the reaction between the Al and C requires a high initial temperature, and this is supplied by the burning C and Al in contact with the air.

Method 2.—Some of the mixture was placed in a 5 × 8 inch test-tube and the top drawn out to a fine capillary tube. The mixture was then heated till red-hot, but no apparent change occurred, even after the whole of the mixture was red-hot. On looking the Al powder was quite visible and the mixture appeared unchanged. Only a very slight evolution of gas was obtained by allowing the mixture to stand over water all night. It is evident that sugar carbon in this state of fineness, and with air excluded, does not combine with Al at a red heat.

Method 3.—Some of the mixture was heated in an open porcelain crucible over a Bunsen burner. The mixture slowly burnt at the surface and finally became incandescent. The mixture was entirely changed, no Al being visible, and a gas was slowly evolved on treating some of it with water.

Method 4.—A sample was placed in a Hessian crucible and covered as in previous experiments. It was heated in the muffle for two hours at 1000°—1100° C. On removal and cooling the contents were found to be solid, no Al visible, und the core consisted of a mass of yellowish crystals.

The reaction between sugar carbon and aluminium powder is not nearly so striking as that between wood charcoal, due probably to (1) the superior hardness and compactness of the sugar charcoal; (2) the non-porosity of the carbon preventing the occlusion of air; (3) the powder not being in such a finely divided state; and (4) the absence of possible helpful impurities, *e.g.*, Fe_2O_3.

Mixtures 4 Al + 8 C.—This mixture could not be made to react in the cold, but on placing in the muffle reaction started, and on withdrawing and cooling a sample of carbide was obtained which reacted with water most vigorously. Samples were therefore made by heating mixture in closed crucible for half an hour. The resulting product was quite soft and black, with patches of yellow crystalline masses.

Mixtures of 8 Al + 3 C.—This mixture would not react in the cold, but did so easily in the muffle. Samples were therefore made as above. The resulting mass was found to be very hard and extremely difficult to remove.

* A Paper read before the Faraday Society, April 28, 1908.

Analyses.

Sample.	Percentages. Free C.	Free Al.	AlN.	Al_4C_3.	Al_2O_3.
A. 4Al + 3C :—					
Top layer.. ..	9·04	1·00	13·93	24·78	52·25
Middle layer ..	9·57	1·75	18·05	34·39	36·24
Lower layer ..	9·25	1·75	40·59	20·05	28·36
B. 4Al + 6C	25·05	1·00	15·04	27·74	31·22
C. 8Al + 3C	6·08	3·62	24·68	46·18	19·44

Analyses of Gas.

Sample 1.—77·9 per cent CH_4, 18·0 per cent H, 4·1 per cent N.

Sample 2.—79·6 per cent CH_4, 17·5 per cent H, 2·9 per cent N.

Sample 3.—75·9 per cent CH_4, 18·3 per cent H, 5·8 per cent N.

SERIES III.—*Aluminium Powder and Graphite.*

Commercial graphite was used, which was found to be very impure and to readily react with Al powder in the cold. On igniting the commercial substance a brown ash was left which amounted to 50·1 per cent of substance taken.

Boiling for twelve hours with conc. HCl gave a product which still yielded 47·3 per cent of ash on ignition. The graphite obtained by treatment with conc. HCl was boiled for six hours with HF, and after this still yielded an ash of 15 per cent.

The partially purified graphite was now treated in an iron tray with fused NaOH for three hours, extracted with water, filtered, digested with conc. HCl, filtered, washed, and dried; after this treatment the ash was less than 1 per cent.

It was found that the original graphite could be purified by two successive fusions with NaOH. During the fusion H was evolved.

None of the mixtures of graphite and aluminium would react in the cold, but those in the proportion 4 Al to 3 C reacted with a fuse when heated to about 300° C. The action was brought about in each case by heating in the muffle, but the action was not so complete and vigorous as with the other forms of C.

The mixture 8 Al + 3 C gave a solid mass containing a yellow crystalline portion. (See Note to "Analysis"). This yellow crystalline formation was seen more or less in all the samples.

Analysis.

Sample.	Percentages. Free C.	Free Al.	AlN.	Al_4C_3.	Al_2O_3.
A. 4Al + 3C (yellow crystals). ..	15·2	0·25	20·04	10·68	53·83 (Note)
B. 4Al + 6C	26·78	0·5	17·52	33·69	21·51
C. 8Al + 3C	7·93	2·3	42·16	36·58	11·11

NOTE.—Dr. Seligman (*Trans. Faraday Society*, vol. iii., p. 8) calls attention to the existence of yellow crystals in the mass produced when Al burns in air, and suggests that they are crystals of Al_2O_3; the authors find that the yellow crystalline portions of their products are always high in Al_2O_3.

Gas Analysis.

1. Sample taken one and a-half hours after starting :— 80·9 per cent CH_4, 16·9 per cent H, 2·2 per cent N.
2. Another sample one hour after :—77·1 per cent CH_4, 21·8 per cent H, 1·1 per cent N.

SERIES IV.

Some experiments were carried out to see the influence of the air and of N in the combination of Al and C under the conditions already described. The mixture of 4 Al + 3 C (wood C) were used.

1. *Heated in a Current of Air.*—Reaction proceeded before tube was visibly hot and proceeded vigorously. Product contained a very large amount of Al_2O_3 and 1·35 per cent of AlN.

2. *Heated in a Current of* N *in Glass.*—Mixture was heated to dull redness, no visible action was seen. The product contained large amount of free C + Al and 3·517 per cent AlN.

3. *Heated in Current of* N *in Berlin Porcelain Tube.*—The tube was heated to full red heat. Reaction had taken place to a greater extent than in 2. It contained 10·46 per cent AlN.

4. *Mixture Heated* in vacuo.—The mixture was placed in a piece of steel bicycle tubing and connected to a Töpler pump. A very slight leak occurred at the joint between the glass and the steel tube, and it is probably due to the small amount of air thus left (the pressure was less than 2 cm. during the heating) that action took place. The tube was heated in a small Fletcher furnace to a bright red heat for twenty minutes.

The product appeared almost unchanged, and where the powder had agglomerated portions were picked out, ground up, sieved, and analysed.

The analysis gave :—

Free C 23·44 per cent, Free Al 65·01 per cent, AlN 1·6 per cent, Al_2O_3 7·0 per cent, Al_4C_3 2·95 per cent.

The authors are of opinion that if air had been rigorously excluded very little action would have taken place. They hope to repeat this experiment again.

NOTE.—*Action of Magnesium and Carbon.*

Some experiments have been carried out on the direct combination of Mg and C, and evidence has been obtained, which the authors are now confirming, that a carbide of magnesium is produced under similar conditions to those described for Al and C.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 2nd, 1908.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

MESSRS. H. Bassett, jun., H. T. Clarke, and C. Dickinson were formally admitted Fellows of the Society.

It was announced that the Council had appointed the following Committees for 1908-1909 :—

Finance Committee—Messrs. E. G. Hooper, G. T. Moody, T. E. Thorpe, W. A. Tilden, and the Officers.

House Committee—Messrs. W. R. Dunstan, J. E. Reynolds, W. J. Russell, J. M. Thomson, T. E. Thorpe, W. A. Tilden, and the Officers.

Library Committee—Messrs. E. C. C. Baly, B. H. Brough, F. D. Chattaway, B. Dyer, A. Harden, C. A. Keane, A. Lapworth, E. J. Mills, J. M. Thomson (Chairman), J. A. Voelcker, J. Wade, the Editor, and the Officers.

Publication Committee—Messrs. E. C. C. Baly, W. R. Dunstan, J. T. Hewitt, R. Meldola, G. T. Morgan, T. E. Thorpe, J. Wade, and the Officers.

Research Fund Committee—Messrs. G. T. Beilby, P. F. Frankland, A. D. Hall, G. Matthey, R. Meldola, R. Messel, W. H. Perkin, J. E. Reynolds, W. A. Tilden, Sir A. Pedler, and the Officers.

Certificates were read for the first time in favour of Messrs. Donald Francis Blyther, B.Sc., 77, Knights Road, Silvertown, E.; Henry Brougham Hutchinson, Ph.D., Ashby Villa, Devonshire Road, Harpenden; Stanley Allen Warrington Okell, 27, King's Road, Ealing, W.; John Day Speed, Mill House, Enfield Lock, Middlesex.

Certificates have been authorised by the Council for presentation for ballot under By-law 1. (3) in favour of Messrs. Cyril Arden Hinds, 724, Russell Street, Bristol, Tenn.,

U.S.A.; William Seelhorst, Eastern Smelting Co., Ltd., Penang, Straits Settlements.

Of the following papers, those marked * were read:—

*72. "*Rate of Hydrolysis of Chloroacetates, Bromoacetates, and α-Chlorohydrin by Water and by Alkali, and the Influence of Neutral Salts on the Reaction Velocities.*" (Preliminary Note). By GEORGE SENTER.

In a former paper (*Trans.*, 1907, xci., 460), the results of an investigation of the rate of hydrolytic decomposition of certain chloroacetates by water and by alkali were given, and the effect of certain neutral salts on the rate of reaction was discussed. The rate of displacement of halogen by hydroxyl under different conditions has now been investigated for bromoacetic acid and sodium bromoacetate and for α-chlorohydrin, and the effect of certain neutral sodium salts on the reaction velocities has been examined.

Bromoacetic Acid.—The reaction represented by the equation $CH_2Br{\cdot}CO_2H + H_2O = HO{\cdot}CH_2{\cdot}CO_2H + HBr$ is unimolecular, and the value of $k = 1/t \log C_0/C_t$ is 0·0062 at 102°, as compared with $k = 0{\cdot}00048$ for chloroacetic acid under equivalent conditions. The reaction is slightly retarded by hydrogen bromide.

Sodium Bromoacetate.—The reaction—

$$CH_2Br{\cdot}CO_2Na + H_2O = HO{\cdot}CH_2{\cdot}CO_2H + NaBr$$

is unimolecular in dilute solution; the value of $k = 1/t \log C_0/C_t$ at 102° is 0·020. The hydrolysis of this salt by alkali, represented by the equation $CH_2Br{\cdot}CO_2Na + NaOH = HO{\cdot}CH_2{\cdot}CO_2Na + NaBr$, is bimolecular, and at 70·4° $k = \frac{1}{tC_0} \cdot \frac{C_t}{(C_0 - C_t)}$ has the value 0·0314 when referred to a N/10 solution.

Effect of Temperature.—The average velocity quotients for a rise of temperature of 10° between the limits of temperature given are as follows:—Chloroacetic acid and water (70—100°), 2·6; sodium chloroacetate and water (70—100°), 3·2; sodium chloroacetate and hydroxide (70—100°), 2·5; bromoacetic acid and water (70—100°), 2·4; sodium bromoacetate and water (70—100°), 2·9; sodium bromoacetate and hydroxide (30—70°), 2·75. The fact that the temperature-coefficients of the hydrolysis of sodium chloroacetate by wa er and by alkali are different, shows that the assumption often made, that the OH′ ions in the latter case act in a catalytic manner, is not justified, and supports the views on the mechanism of the reactions advanced in the previous paper (*loc. cit.*).

α-Chlorohydrin.—The hydrolysis of α-chlorohydrin by water alone is extremely slow; the value of $k = 1/t \log C_0/C_t$ is 0·00010 at 101°. Hydrochloric acid retards the reaction slightly. In the presence of alkali the change is extremely rapid; the value of k for the bimolecular reaction represented by the equation—

$$HO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl + NaOH = HO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH + NaCl$$

is 0·052 at 0°, referred to a N/10 solution as unit.

Effect of Neutral Salts.—Neutral sodium salts slightly retard the hydrolysis of chloro- and bromo-acetates by water, they greatly accelerate the hydrolysis of these compounds by alkali, but have practically no effect on the rate of reaction between α-chlorohydrin and alkali. The accelerating effect of molar concentrations of different salts on 0·1 molar solutions of chloro- or bromo-acetates and alkali is represented in the table, the rate of the reaction in the absence of neutral salts being taken as unity.

Sodium Chloroacetate and Hydroxide at 70·4°.

Neutral salts.	Ratio of velocities.
None	1·0
$NaNO_3$	1·55
NaCl	1·55
$NaClO_3$	1·55
$\frac{1}{2}Na_2SO_4$	1·55
$CH_3{\cdot}CO_2Na$	1·58
$H{\cdot}CO_2Na$	3·3

Sodium Bromoacetate and Hydroxide at 70·4°.

Neutral salts.	Ratio of velocities.
None	1·0
$NaNO_3$	1·53
NaBr	1·53
$NaClO_3$	1·53
$H{\cdot}CO_2Na$	2·8

The effect of sodium nitrate on the reaction between sodium chloro-acetate and hydroxide is of the same magnitude, within the limits of experimental error, at 55° and 101°.

The above results confirm the views on neutral salt action advanced in the previous paper, that the effect in question is mainly due to the action of the salt on the reacting substances, and appear to be incompatible with the hypothesis advocated from time to time by different observers, most recently by Armstrong and his co-workers (*Proc. Roy. Soc.*, 1907, lxxix., A, 586), that neutral salt action is due to combination between salt and solvent, with consequent concentration of the solution.

DISCUSSION.

Mr. JEFFERS asked if Dr. Senter assumed that the pressure developed in the sealed tubes had no influence whatever on the velocity of hydrolysis. Pressure was known to have a large influence in the case of the hydrolysis of carbohydrates, and it seemed impossible to correlate the figure given for the velocity unless the pressure was known in all cases.

Dr. SENTER, in reply, pointed out that, according to the experiments of Röntgen (*Ann. Physik.*, 1891, xlv., 98; compare also Rothmund, *Zeit. Phys. Chem.*, 1896, xx., 170), the effect even of great changes of pressure on the rate of a reaction was very slight. In the case most fully investigated, a change of pressure from 1 to 500 atmospheres increased the rate of the reaction by 1 per cent. As in the present experiments the highest pressure in the sealed tubes was 2 atmospheres and the variations less than 1 atmosphere, it was obvious that the effect in question was quite negligible.

*73. "*The Constituents of Cyprus Origanum Oil. Isolation of a New Terpene 'Origanene.'*" By SAMUEL SHROWDER PICKLES.

The essential oil yielded by the principal origanum plant of Cyprus has been examined, and found to consist mainly of carvacrol (84 per cent). There are also present—(1) a hydrocarbon, $C_{10}H_{16}$, apparently a new terpene, for which the name *origanene* is proposed (2·5 per cent); (2) cymene, which, together with associated terpenes (b. p. 170—180°), constitutes 8·5 per cent; (3) terpene alcohols (3·5 per cent); and (4) high boiling residue (1·3 per cent) besides very small quantities of a second phenol which gives a purple coloration with ferric chloride, and a volatile acid, probably *iso*butyric acid.

The results of experiments on the constitution of the hydrocarbon "origanene" lead the author to conclude that the terpene is probably $\Delta^{1:3}$-p-*menthadiene*, $CMe\lessdot^{CH-CH}_{CH_2{\cdot}CH_2}\gtrdot C{\cdot}CHMe_2$.

*74. "*The Displacement of Halogen in l Phenylchloroacetic Acid by Hydroxy- and Methoxy-groups. A Contribution to the Chemistry of the Walden Inversion.*" By ALEX. MCKENZIE and GEORGE WILLIAM CLOUGH.

The authors have resolved *r*-phenylchloroacetic acid into its optically active components by means of morphine in methyl-alcoholic solution.

The action of water on *l*-phenylchloroacetic acid, the action of water on sodium *l*-phenylchloroacetate, the action of aqueous sodium hydroxide on sodium *l*-phenylchloroacetate, the action of water on silver *l*-phenylchloroacetate, the action of silver carbonate on *l*-phenylchloroacetic acid, and the action of methyl-alcoholic sodium methoxide on *l*-phenylchloroacetic acid have been examined with reference to the Walden inversion.

DISCUSSION.

Dr. SMITH, referring to the fact that *d*-chlorosuccinic acid is converted by sodium hydroxide into *l*-malic acid and by silver oxide into *d*-malic acid, stated that Walden assumes that the inversion, which must have occurred during one of these changes, takes place in the second reaction. In view of Dr. Senter's result, that sodium chloroacetate and sodium hydroxide react ionically, the converse would seem to be more probable, for during the reaction between sodium hydroxide and *d*-chlorosuccinic acid, which by analogy is ionic, there would be a greater possibility for change of configuration to occur than in the reaction between *d*-chlorosuccinic acid and silver oxide, which would be a case of simple substitution.

Dr. MCKENZIE stated that Walden regarded the change

$$d\text{-}CO_2H\cdot CH_2\cdot CHCl\cdot CO_2H \rightarrow l\text{-}CO_2H\cdot CH_2\cdot CH(OH)\cdot CO_2H$$

by means of potassium hydroxide as, in all probability, optically normal, because the rotation of the malic acid formed is of the same sign as that of the malic acid from which *d*-chlorosuccinic acid is formed by the action of phosphorus pentachloride.

Fischer had pointed out (*Ber.*, 1907, xl., 490) that the view that silver oxide acts abnormally, whilst potassium hydroxide acts normally, may appear somewhat strange to many chemists.

75. "*The Condensation of Epichlorohydrin with Phenols.*" By DAVID RUNCIMAN BOYD and ERNEST ROBERT MARLE.

The authors find the statements of Cohn and Plohn (*Ber.*, 1907, xl., 2597) with regard to the products obtained by the action of epichlorohydrin on alkaline solutions of phenol and *p*-cresol to be incorrect. The crystalline compound (m. p. 81—82°) which is obtained from phenol and epichlorohydrin, and which is stated by Cohn and Plohn to be phenyl glycide ether, $C_6H_5\cdot O\cdot CH_2\cdot CH\langle^{CH_2}_{O}\rangle$, is really glyceryl diphenyl ether,—

$$C_6H_5\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot O\cdot C_6H_5.$$

Phenyl glycide ether is an oil boiling at 133° under 23 mm. pressure.

Similarly, the crystalline compound (m. p. 88°) obtained from *p*-cresol and epichlorohydrin is the glyceryl di-*p*-tolyl ether, $C_7H_7\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot O\cdot C_7H_7$, and not the *p*-tolyl glycide ether.

The authors have prepared *phenoxydichloropropane*, an oil boiling at 139—140° under 13 mm. pressure.

76. "*A New General Method of Preparing Diazonium Bromides.*" By FREDERICK DANIEL CHATTAWAY.

Primary aromatic hydrazines react quantitatively with the diazonium perbromides producing diazonium bromides, thus :—

$$2\ \begin{matrix}R\cdot N\cdot Br\\ |\\ Br\cdot N\cdot Br\end{matrix} + \begin{matrix}R\cdot N\cdot H\\ |\\ H\cdot N\cdot H\end{matrix} = 3\ \begin{matrix}R\cdot N\cdot Br\\ |\\ H\cdot N\cdot Br\end{matrix} + 3\ \begin{matrix}R\cdot N\cdot Br\\ \|\\ N\end{matrix} + 3\ HBr$$

As the diazonium perbromides are so easily obtained in the solid state by adding bromine to aqueous solutions of diazonium salts, and as they can be kept in a dry atmosphere for a long time without alteration and are comparatively safe to handle, this reaction affords a very convenient method for preparing diazonium bromides in the solid state.

For this purpose it is only necessary to suspend the finely powdered perbromide in alcohol and, after cooling, to add the calculated quantity of the corresponding hydrazine also dissolved in alcohol and cooled. The solid diazonium bromide is at once formed, and, after adding an equal bulk of ether to complete the deposition, can be collected in a pure state.

The reaction is a general one, and takes place readily and quantitatively with all primary aromatic hydrazines and perbromides that have been studied.

77. "*The Absorption Spectrum of Triphenylmethane.*" By ALFRED GODFREY GORDON LEONARD.

In order to ascertain the cause of the difference between the absorption curve plotted by Hartley, in 1887, and that plotted by Baker, in 1907, the absorption spectrum of triphenylmethane was thoroughly re-examined.

All the specimens examined gave at first curves similar to that obtained in 1887, but, on purifying the samples by repeated recrystallisation from alcohol, the absorption curve became identical with that found by Baker. This curve is therefore the true absorption curve of triphenylmethane.

The difference is clearly shown to be caused by the presence of an impurity in the sample originally examined, and this impurity is always present when the triphenylmethane is prepared from benzene and chloroform by Friedel and Crafts' reaction (see following abstract).

78. "*The Nature of the Impurity found in Preparations of Triphenylmethane.*" By WALTER NOEL HARTLEY.

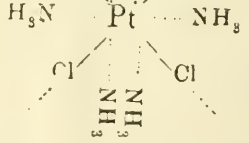
The experiments of Mr. A. G. G. Leonard have shown conclusively that in the preparation of triphenylmethane there are always two substances obtained, even when the materials are of the greatest purity and free from moisture.

The second substance must be a hydrocarbon ; it is yellow, and apparently it undergoes oxidation, becoming still brighter in colour. From these and other considerations it appears to be identical with Gomberg's triphenylmethyl, and the final product with triphenylmethyl peroxide.

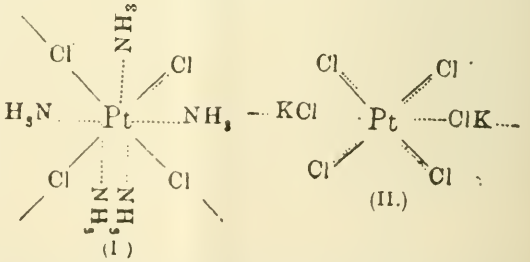
79. "*The Constitution of Co-ordinated Compounds.*" By SAMUEL HENRY CLIFFORD BRIGGS.

An attempt has been made to devise formulæ for co-ordinated compounds which will fulfil the requirements of the experimental results of Werner and his colleagues, and also give some idea of the manner in which the affinities of the atoms are disposed within the molecule.

The existence of the two compounds $(Pt6NH_3)Cl_4$ and $(PtCl_6)K_2$, in which the platinum atom is the basis of a complex cation and anion respectively, suggests the view that the platinum atom has both positive and negative affinities (compare Berzelius, Abegg, and others). Assuming that every element has two kinds of affinity, $(Pt6NH_3)Cl_4$, may be written :—



in which the saturation of the positive affinity of the platinum (situated at the centre of an octahedron) is expressed by a straight line, and the saturation of the



(I.) (II.)

negative affinity by a dotted line. On removing one molecule of ammonia and saturating the negative affinity

of the platinum thus liberated by the free positive affinity of one of the chlorine atoms, we obtain (I). Similarly, $(PtCl_6)K_2$ is represented by (II.).

These bonds are intended to represent the saturation of affinities only, and no assumptions are made with reference to the valencies of the atoms in question.

The formulæ were discussed from the point of view of the electrolytic dissociation of the compounds, and it is suggested that the non-ionisable chlorine atom in the compound $(Pt_5NH_3Cl)Cl_3$ is the one which has both the negative and positive affinities saturated as expressed in the formula given above.

In the salts with a complex anion, these formulæ suggest the possibility of isomerism due to differences in the points of attachment of the positive atoms. The cases of isomerism in compounds with an anionic complex, which are referred to by Werner (*Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*), can thus be satisfactorily explained.

80. "*A Combined Stopcock and Capillary Connecting Tube for Gas Burettes.*" By Arthur Edwin Hill.

The familiar method of connecting a Hempel burette to the absorption pipette by means of a short piece of thick-walled glass capillary tubing bent twice at right angles and two short pieces of thick rubber tube is very unsatisfactory, as it is liable to give inaccurate results, and requires a great deal of attention.

Before commencing an absorption, the air, entrapped in the capillary tubes and rubber connexions, should be expelled; as this operation is rather troublesome, it is often not properly effected. Again, when absorption is complete in the pipette and the gas is returned to the measuring burette, the absorbent should be allowed to flow back as far as the capillary tube at the top of the burette, but, since this adjustment has to be made when the thread of absorbent is out of sight behind the rubber connexion, some of it often finds its way into the burette before the pinchcock can be closed.

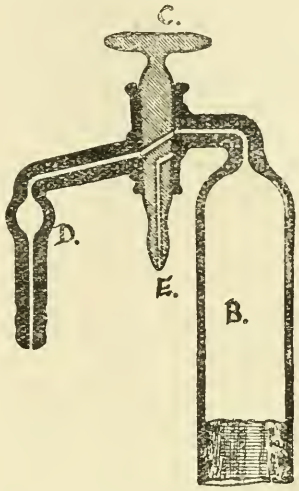
The combined stopcock and capillary connecting tube indicated in section in the figure is sealed to the top of the measuring burette B. The three-way stopcock C in addition to controlling the flow of gas from the burette, also affords a means of connecting the pipette with the outside air through the bottom outlet E when it is attached to the burette.

The burette is connected to the pipette by a short piece of thick rubber tube, which is slipped over and well wired to the end of the capillary connecting tube and to the capillary tube of the pipette.

To expel the air entrapped in the capillary tubes and rubber connexion, a piece of rubber tube is slipped over the bottom outlet E of the stopcock C, and the stopcock is turned to make connection between the pipette and the outside air; the air is then sucked out through the tube, and the absorbent fills the vacant space. The stopcock is closed by giving it a half turn, so that the handle is in a plane at right angles to that of the connecting tube. In order to connect the burette with the pipette, the stopcock is given another half turn in the same direction as before. The barrel of the stopcock is pierced in a way which makes it impossible to connect the burette with the outside air through the bottom outlet E, a source of accidental error being thereby eliminated.

When absorption is complete and the gas is returned to the burette, the absorbment is allowed to flow back as far as the stopcock C, which is quickly closed to prevent it from flowing any further. The bulb D facilitates this adjustment by retarding the advance of the absorbent before it reaches the stopcock; it also prevents the drops of absorbent, which often lodge in the rubber connexion, from passing over with the gas into the burette.

Before the pipette is disconnected from the burette, the stopcock is turned back to the position which will connect the pipette with the outside air, and the thread of absorbent is allowed to flow back into the pipette. They are then disconnected, and those parts of the capillary connecting tube and stopcock which have been in contact with the absorbent can be washed with water and subsequently dried in a current of warm air without in any way affecting the contents of the burette.



Subsequent absorptions are effected by a similar procedure.

(We are indebted to the author for permission to use the woodcut illustrating this paper).

(To be continued).

SOCIETY OF CHEMICAL INDUSTRY.

(London Section).

Ordinary Meeting, May 4th, 1908.

Dr. J. Lewkowitsch in the Chair.

"*The Manufacture of Sodium Nitrite.*" By Gilbert T. Morgan.

The various processes for preparing sodium nitrite are reviewed, and an account is given of the manufacture of the salt by the lead and sulphur processes. Experiments are described bearing on the production of sodium nitrite from calcium nitrate.

"*On some Simple and Mixed Esters of Cellulose. The Alkaline Decomposition of Nitro-Derivatives of Cellulose and other Carbohydrates.*" By Watson Smith, jun.

The action of acid mixtures containing acetic anhydride and nitric acid with and without the addition of concentrated sulphuric acid as a dehydrating agent was investigated. Pure nitrocelluloses and aceto nitrocelluloses were in this way prepared.

Pure acetyl nitrate acts on cellulose with the production of nitrocelluloses containing a high percentage of nitrogen.

Acetyl nitrocelluloses were obtained by the action of acetic anhydride and sulphuric acid on nitrocellulose. These new bodies give well characterised compounds with phenylhydrazine.

The nitro-derivatives of cellulose, starch, glucose, and fructose were treated with alcoholic caustic soda. In each case products of partial denitration were isolated; thus from gun-cotton was obtained tetra-nitrocellulose, from which acetyl and phenylhydrazine derivatives were prepared. Aldehydic or ketonic acids were isolated from the final decomposition products, and were characterised by their forming well-crystallised compounds with aniline and phenylhydrazine. A close relationship is shown in this way to exist between cellulose, glucose, and levulose.

"*The Mechanism of Filtration.*" By E. HATSCHEK.

The structure of the solid deposit on the filtering surface is shown to be determined by the flow of the liquid into the latter, and to be independent of the pressure, which therefore does not affect the percentage of voids. The velocity of flow through a porous septum with varying pressure is discussed and illustrated by curves showing a maximum loss of head at a pressure characteristic for each septum. Various types of the latter are examined and classified according to their rigidity.

A number of the more important precipitates are shown in photo-micrographs, to illustrate crystalline, amorphous, and aggregated particles.

The effect of the method of precipitation on the nature of the precipitates is also shown, and the author urges the microscopic examination of such, and the systematic search for a method of precipitation giving the result best adapted for the subsequent process of filtration.

"*Metanil Yellow; Its Use as a Selective Indicator.*" By E. LINDER.

The author finds that filter-paper dyed with metanil yellow is turned violet on exposure in the dry state to fumes of mineral acids, while no effect is produced upon the paper by sulphur dioxide, chlorine, sulphuretted hydrogen, or acetic acid.

The test-paper can therefore be applied selectively for the identification of mineral acid in gaseous mixtures.

The violet compounds so obtained are characterised by marked differences of stability in contact with atmospheric moisture, the compounds being unstable in proportion as the mineral acid is volatile. This property is made use of for differentiating between certain mineral acids.

The test-paper can also be applied for the detection of "mineral acid" in adulterated vinegar:—A drop of the liquid is placed on the test-paper, which is then re-dried at 80° to 90° C. If "mineral acid" is present, the paper assumes a violet tint, the depth of which is proportionate to the amount of "mineral acid."

"*Conversion of Oleic Acid into Candle Material.*" II. By J. LEWKOWITSCH, M.A., Ph.D.

In a continuation of a paper read eleven years ago on the same subject the author discussed the efforts made by a number of inventors to convert oleic acid into stearic acid by means of sulphuric and by the aid of the electric current. A new solution of the problem seemed to lie in the application of the classical work of Sabatier and Senderens, in 1902, to oleic acid, and since then a number of workers have endeavoured to carry into effect the reduction of oleic acid to stearic acid. The author has succeeded in converting oleic acid, in practically quantitative yield, to stearic acid, and showed samples of the product. Several patent specifications, also modifications of the original catalytic process of Sabatier, were referred to.

FARADAY SOCIETY.

Ordinary Meeting, April 28th, 1908.

Prof. A. K. HUNTINGTON, Vice-President, in the Chair.

THE following nominations for the Officers and Council to be elected at the Annual General Meeting were announced:—

President—Sir Oliver Lodge, F.R.S.

Vice-Presidents—G. T. Beilby, F.R.S.; R. A. Hadfield; Geh. Reg.-Rat. Prof. W. Hittorf; Prof. A. K. Huntington; Lord Rayleigh, O.M., P.R.S.; Prof. A. Schuster, F.R.S.; Prof. J. J. Thomson, F.R.S.

Treasurer—F. Mollwo Perkin, Ph.D.

Council—Bertram Blount, F.I.C.; A. C. Claudet, M.I.M.M.; S. Z. de Ferranti, M.I.E.E.; F. W. Harbord, F.I.C.; R. S. Hutton, D.Sc.; T. M. Lowry, D.Sc.; H. F. K. Picard, M.I.M.M.; James Swinburne, F.R.S.; J. F. L. Vogel, M.I.E.E.; N. T. M. Wilsmore, D.Sc.

A paper by Prof. A. K. HUNTINGTON and C. H. DESCH, D.Sc., Ph.D., on "*The Planimetric Analysis of Alloys, and the Structure of Phosphor-copper,*" was read by Prof. HUNTINGTON. Dr. T. M. Lowry occupied the Chair during the reading of the paper, which was illustrated by means of lantern-slides.

The authors discuss the conditions under which it is possible to estimate the relative proportions of the constituent metals of an alloy by means of a planimetric measurement of the areas of the solid phases exposed in a polished and etched micro-section. Details of the method are given, and its accuracy is shown by a series of measurements of analysed alloys. The method has been most fully studied in the case of phosphor-copper, of which a number of photo-micrographs are shown. In the case of alloys containing less than the eutectic proportion of phosphorus, however, the area of the copper crystals is found to be considerably greater than that calculated from the composition determined by analysis. The origin of the discrepancies was traced to the segregation of the eutectic, the copper crystals which separate at first drawing to themselves a portion of the copper of the surrounding eutectic. The crystals are therefore surrounded by a belt of copper phosphide. By measuring the area of this belt and thence calculating the amount of segregated copper, a correction may be applied to the area of the crystals, and a very satisfactory agreement with the analytical results is thus obtained.

Prof. W. W. HALDANE GEE (communicated) suggested that the method might be used to compare the relative losses of the constituents of an alloy after prolonged etching with different reagents, or after electrolytic corrosion, and so throw light on the method of corrosion.

Dr. C. H. DESCH stated, in reply to a question, that the method could not be of quite general applicability, it being useless, for example, in cases where the alloy was homogeneous. It was also necessary for the alloy to be in a state of physical equilibrium.

Prof. A. K. HUNTINGTON added that the method would probably be usefully extended to the case of the phosphor-tin alloys.

A paper on "*The Interaction of Aluminium Powder and Carbon,*" by FRANK E. WESTON, B.Sc., and H. RUSSELL ELLIS, B.Sc., was read in abstract by Mr. WESTON. (See CHEMICAL NEWS, xcviii., p. 219).

Dr. F. MOLLWO PERKIN did not agree with the authors' view as to the cause of the reaction. There was no evidence that at 1100° CO could be reduced. Possibly the reaction was started by superficial oxidation of the aluminium.

Mr. CHARLES WEISS referred to the aluminium carbides found at the bottom of the furnaces in which aluminium is made. As a rule these carbides were entirely enclosed in a coating of alumina.

Mr. H. R. ELLIS gave some further particulars regarding the nitride produced, probably by the action of nitrogen at a high temperature on the aluminium carbide. As crude aluminium carbide can be made by heating clay and carbon in the electric furnace, this method might be as economical a one for the fixation of atmospheric nitrogen as the combination of calcium carbide and nitrogen to form cyanamide.

Prof. A. K. HUNTINGTON suggested that perhaps the authors' reaction was a triple one, brought about by the presence of a gas (CO_2 or CO) between two solids which would not react alone. The gas, unlike the carbon, might be able to permeate the film of oxide surrounding the aluminium, getting at the actual metal, and so start the reaction.

A Note on "*Technical Chemistry in Russia*" was communicated by Prof. N. PILTSCHIKOFF.

The paper refers to copper-refining works at Moscow and St. Petersburg and the Laschinsky electrolytic method of copper recovery from its ore which is used at Boleslav. The special feature of the process is to prevent oxidation

of iron at the anodes. and consequent waste of current by coating these with lead. The Gorbov and Mitkievitch arc furnace for the fixation of atmospheric nitrogen is about to be worked on a technical scale. In this the current of air draws the arc (the voltage across which is 600—1500, direct or alternating) into a worm, in whose mouth is formed a "bunch of fire" through which all the air has to pass. The products of combustion are subsequently cooled in the further part of the worm. In an experimental 14-kw. furnace an output of 56 grms. HNO_3 per kw.-hour has been attained. The furnace is stated to be simpler and more economical than the Birkeland-Eyde furnace. Other processes mentioned are the late Prof. Kloboukoff's method of electric tanning, which prevents fermentation in the bath, and Dr. Danilevsky's process for depositing copper on leather. The purification of water by ozone is being experimented with at St. Petersburg, and at Moscow Prof. Sokotoff's powerful and economical ozoniser is being tried.

NOTICES OF BOOKS.

Thermochemistry. By Julius Thomsen. Translated from the Danish by Katharine A. Burke, B.Sc. (Lond.). London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1908.

The original Danish edition of this work was an abridgment of the author's complete treatise on thermochemistry, entitled "Thermochemische Untersuchungen," which was published during the years 1882-1886. This treatise gives an account with full experimental details of all the investigations carried out by Prof. Thomsen, and is the most comprehensive work on the subject extant. In order to render the results of his investigations and the conclusions to be drawn from them more accessible, he published more recently the numerical and theoretical results without the minute descriptions of the experiments in a shorter book, of which this volume of the Text-books of Physical Chemistry is a translation. The illustrations of the apparatus used for typical determinations are sufficient to give a clear idea of the general experimental methods, while comparative tables of numerical results show the quantitative relations which have been determined. The value of the theoretical parts of the book is to some extent lessened, because Prof. Thomsen's work was published before the theory of ionisation had been introduced into chemistry, but the translator has added notes in many cases to point out the modern interpretation of the facts recorded. In Part I. of the book the thermochemistry of aqueous solutions is discussed; Part II. deals with the compounds of the non-metals among themselves; and Part III. with the compounds of the metals and non-metals. In the fourth part the heat phenomena of organic compounds are described, and it is shown that, as with inorganic substances, the chemical reactions of the carbon compounds are based upon the tendency of the atoms to attain a state of stable equilibrium.

Uebersicht über die Deutschen Reichspatente betreffend Heilmittel und Desinfektionsmittel. ("Survey of the German Patents dealing with Remedies and Disinfectants"). By Dr. E. A. Franz Düring. Gräfenhainichen: C. Schulze and Co. 1908.

This book contains short abstracts of the specifications of recent patents dealing with disinfectants, &c., which have been taken out in Germany. Patents which have recently run out are also included, and the little book will be a useful addition to the library of the inventor or manufacturer of disinfectants. Its value would be greatly increased if an index were provided.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 11, March 16, 1908.

Hydrates of Arsenic Acid.—M. Auger.—The hydrate, $(AsO_4H_3)_2H_2O$, possesses an appreciable dissociation tension below 0°, and loses water even at −10°. At about 12° this loss of water ceases with the formation of the hydrate, $As_3H_{10}O_5$ or $As_2O_7H_4.AsO_3H$. Above 12° and up to 148° the composition of the hydrate obtained in a desiccating medium approximates closely to $As_3H_{10}O_5$. This is dehydrated completely between 180° and 440°, and above 440° it begins to lose oxygen.

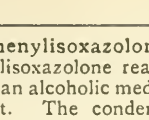
No. 12, March 23, 1908.

Absorption Spectra of Crystals of the Rare Earths Salts and their Modification in a Magnetic Field at the Melting-point and Boiling-point of Hydrogen.—Jean Becquerel and H. Kamerlingh Onnes.—The absorption bands of the crystals of the rare earth salts become narrower as the temperature is lowered, until at −190° the width of the bands is proportional to the square root of the absolute temperature. At lower temperatures most of the bands do not follow such a simple law. At the temperature of liquid air almost all the absorption bands of the compounds of the rare earths are much more intense than at the ordinary temperature. For every band there exists a temperature at which the absorption reaches a maximum. When the optical axis of a uniaxial crystal is oriented parallel to the magnetic field and to the beam of light, the distance apart of absorption bands of right and left vibrations remain invariable in the same magnetic field till −259°. The changes of frequence, under the action of magnetism, of oscillating systems are to a first approximation independent of the thermic movements, the intensity and width of the bands as well as of the paramagnetic properties of the substance. They seem to be the first cause of diamagnetism. This invariability of changes of frequence provides a confirmation of the hypothesis of positive electrons. With biaxial crystals the inertia of the oscillating systems varies with the direction of the movement.

Action of Chlorine on Dithymol.—H. Cousin.—When a current of chlorine is allowed to act on dithymol, $C_{20}H_{26}O_2$, in suspension in chloroform, dichlorodithymol is first formed, $C_{20}H_{24}Cl_2O_2$; then the halogen acts as an oxidiser, and removes two atoms of hydrogen from this dichloro-compound, yielding dichlorodithymoquinone, $C_{20}H_{22}Cl_2O_2$. Finally, if the action of the chlorine is continued this derivative fixes two atoms of chlorine, and forms a compound, $C_{20}H_{22}Cl_4O_2$. From its reactions it does not appear to be a tetrachloride of dithymol, for it is insoluble in soda, and can be reduced by SO_2 in alcoholic solution, and by powdered zinc to dichlorodithymol. Hence it must be looked upon as the derivative obtained by fixing two atoms of chlorine to the quinone; *i.e.*, as the dichloride of dichlorodithymoquinone.

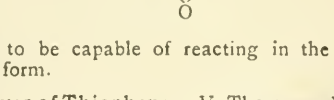
Products of the Action of Aluminium Chloride and Hydrochloric Acid on Benzene.—G. Gustavson.—When benzene containing finely-powdered aluminium chloride is saturated with gaseous hydrochloric acid, a dark brown layer of liquid is formed, which does not mix with the benzene floating on it. The action is very slow, and lasts some weeks, but it can be accelerated by heating. When this dark brown liquid is decomposed by water the products are benzene, a resinous residue, and hydrocarbons, from which, by the action of fuming sulphuric acid and barium carbonate, the barium salt of methylphenylcyclopentane is obtained. The free hydrocarbon may be prepared by decomposing the barium salt with hydrochloric acid in sealed tubes at 180—200°.

Derivatives of Phenylisoxazolone.—A. Wahl and André Meyer.—Phenylisoxazolone readily condenses with aromatic aldehydes in an alcoholic medium with or without a condensation agent. The condensation takes place slowly in the cold, but becomes rapid at the ordinary temperature in presence of a small quantity of piperidine. This condensation seems to show that phenylisoxazolone possesses a methylene group, although Moureu and Lazennec have shown that its constitutional formula is probably—



It appears to be capable of reacting in the tautomeric methylenic form.

Derivatives of Thiophene.—V. Thomas —Magnesium dissolves very easily in thiophene iodide, $C_4H_3SI(\alpha)$, in presence of anhydrous ether, and the magnesium derivative thus formed behaves like phenyl magnesium iodide. It reacts with fatty ketones, giving tertiary alcohols from which ethylene hydrocarbons can be separated. The reaction is apparently—



R = fatty or aromatic radical ; T = thienyl radical. Acetophenone reacts in the same way with thienyl magnesium iodide. Michler's ketone yields a green colouring matter possessing all the properties of thiophene, $[C_6H_4—N(CH_3)_2]_2=C(OH).C_4H_3S$.

MEETINGS FOR THE WEEK.

Tuesday, 19th.—Royal Institution, 3. "Why Light is believed to be a Vibration (2) What is it which Vibrates?" by Prof. F. T. Trouton, F.R.S., &c.

Wednesday, 20th.—Microscopical, 8. Exhibition of Microscopical Aquatic Life.

—— Royal Society of Arts, 8. "Industrial Entomology, or the Economic Importance of a Study of Insect Life," by F. Martin Duncan.

Thursday, 21st.—Royal Institution, 3. "The Chemistry of Photography" by Alexander Scott, F.R.S., &c.

—— Royal Society of Arts, 4.30. "The United Provinces of Agra and Oudh," by Sir James Digges La Touche, K.C.S.I.

—— Chemical, 8.30. "Hydroaromatic Ketones," by A. W. Crossley and C. Gilling. "Titanidihydroxymaleic Acid and the Detection of Titanium," by H. J. H. Fenton. "Some Experiments on Carbon at High Temperatures and Pressures and Apparatus therefor," by R. Threlfall. "The Sulphides and Oxysulphides of Silicon," by I. G. Rankin and S. M. Revington.

Friday, 22nd.—Royal Institution, 9. "Recent Researches in the Structure of the Universe," by Prof. Dr. J. C. Kapteyn, of the University of Groningen.

—— Physical, 5. "The Spectrum Top," by G. P. Sexton. "The Coefficient of Diffusion," by B. W. Clack. "Production of Small Alternating Currents of Variable Frequency suitable for Telephonic and other Measurements," by B. S. Cohen,

Saturday, 23rd.—Royal Institution, 3. "Japanese Prints," by Laurence Binyon.

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THE CHEMICAL NEWS.

Vol. XCVII., No. 2530.

THE FREEZING-POINT OF MILK.

A Method of Detecting Adulteration, with some Considerations of Osmotic Pressures.

By W. R. GELSTON ATKINS.

The maintenance of temperature equilibrium in the animal body has long been studied, and its wonderful constancy in health is well known, but it is only in more recent years that the pressure has been considered. The osmotic pressure of blood was shown by v. Koranyi to be constant in health, a rise in pressure being a sure indication of grave disease. He studied the relation between the blood and urine, using the freezing-point method with a Beckmann thermometer to determine the osmotic pressures. A healthy kidney produces urine the osmotic pressure of which is from two to four times that of the blood. It is a great economy in water for an animal to produce this concentrated solution, but for the sake of this saving the animal has to do work against osmotic forces by means of the specialised tissue in the kidneys.

Consider now the production of milk; here no advantage will occur either to parent or offspring by concentrating the product so as to have a greater osmotic pressure than the blood and body generally. Thus it seems extremely unlikely that any special cells will have arisen in the milk glands, during the course of evolution, for the purpose of effecting this useless concentration. Accordingly, it appears reasonable to expect an upper limit to the osmotic pressure of milk, as shown by a maximum depression of freezing-point, this being the osmotic pressure of the blood. In other words, the freezing-point of milk can never lie below that of the blood of the animal producing it. This anticipation has been borne out by the examination of a hundred samples of milk extending over a period of two months.

Inspection of these results shows that the freezing-point of milk is nearly constant, being usually slightly higher than that of blood. Were the osmotic pressure of the milk much less than that of the blood, salts from the body would be driven into it tending to restore equilibrium. The intake of large quantities of water by the animal does not affect the milk, for the blood is kept at a constant concentration by the action of the kidneys, as in such cases they excrete nearly pure water. As the blood is maintained constant, or almost so, there is no reason why drinking large quantities of liquid should affect the concentration of the milk to a greater extent than it affects the concentration of the blood.

Nevertheless, there are undoubtedly greater variations in the milk than in the blood. This is to be expected, for its absolute constancy is not so important to the life of the animal; it is, as it were, accidentally constant, as the cells secreting it are nourished by a liquid, the blood, the osmotic pressure of which is constant. Now even in milk which has not been tampered with in any way cream may be deficient up to a large percentage of the average quantity. These variations are quite beyond the range of any I have met with in freezing-point determinations, and, indeed, such large variations in the osmotic pressure would be hard to account for. Thus it appears that milk deficient in fat may be of quite normal osmotic pressure, as shown by a normal freezing-point. The fat, of course, has no effect at all on the freezing-point, as it is not in solution, but present merely in minute globules.

Specimens of milk were bought daily from various Dublin dairies, and examined. As these were fairly constant in freezing-point, arrangements were made for obtaining specimens of morning and evening milk daily from the same cows. Specimens were supplied by the Lucan Dairy Co., and the values varied very little. The results are tabulated below. The letters denote Dublin dairies.

Date.	N.	L.	A.	C.	K,
Jan. 25..	−0·550	−0·525	−0·520	—	—
Feb. 6..	0·540	0·510	0·520	—	—
7..	0·520	0·530	0·545	—	−0·530
8..	0·540	0·520	0·520	—	0·550
10..	0·550	0·490	0·490	−0·570	0·570
11..	0·530	0·560	0·570	0·595	0·580
12..	0·570	0·570	0·580	0·580	0·535
13..	0·550	0·545	0·560	—	0·555
14..	0·550	0·550	0·545	0·550	0·575
17..	0·580	0·590	0·555	0·580	—
24..	0·540	0·535	0·545	0·610	—
28..	—	—	—	—	0·570
Mean..	0·55	0·54	0·54	0·56	0·55

Morning and Evening Milk from Four Cows.

	B.		D.	
	6 a.m.	2 p.m.	6 a.m.	2 p.m.
Feb. 24 ..	—	−0·555	—	−0·545
25 ..	−0·535	0·560	−0·570	0·535
26 ..	0·550	0·550	0·540	0·545
27 ..	0·550	0·560	0·550	0·550
28 ..	0·540	0·555	0·555	0·560
29 ..	0·555	—	0·575	—
Mean ..	0·55		0·55	

	J.		S.	
	6 a.m	2 p.m.	6 a.m.	2 p.m.
Mar. 5 ..	—	−0·545	—	−0·560
6 ..	−0·550	0·570	−0·550	0·545
7 ..	0·560	—	0·550	—
8 ..	—	0·545	—	0·530
9 ..	0·560	—	0·540	—
11 ..	0·560	0·540	0·560	0·550
12 ..	—	0·550	0·550	0·550
13 ..	0·560	0·550	0·560	0·550
14 ..	0·560	—	0·560	—
15 ..	—	0·560	—	0·560
16 ..	0·560	—	0·570	—
Mean ..	0·55		0·55	

Dairy Milk.		*Milk of Individual Cows.*	
Mean of N ..	−0·55	Mean of B ..	−0·55
„ L ..	0·54	„ D ..	0·55
„ A ..	0·54	„ J ..	0·55
„ C ..	0·56	„ S ..	0·55
„ K ..	0·56		

Mean of all the samples (96) .. .. −0·55° C.

Thus, the mean freezing-point of cow's milk is −0·55° C., and the value does not usually vary by more than −0·03° C. above or below. Occasionally it may fall to −0·61° C., but not below −0·62° C., the freezing-point of cow's blood; the extreme variation on the other side met with was −0·49° C., which is 0·06° C. above the mean, just as much as the lower limit observed differs from it.

Application of the Freezing-point Method to Detection of Added Water.

It is possible to be perfectly certain whether a sample of milk is genuine by determining its specific gravity and freezing-point, unless it has been scientifically faked so as to give a correct result for the total solids, other than fat or casein, as ordinarily determined. For if the milk is undiluted and unskimmed, both values will be correct; if it is skimmed, the specific gravity will be too high, but the freezing-point will be unaffected, as fats have no effect

upon this; if, however, water has been added to bring the specific gravity to the correct value, the freezing-point will be too high; *i.e.*, will be closer to 0·00 C., the freezing-point of pure water. Water added without skimming can be at once detected by the freezing-point determination, and the amount present quantitatively measured.

Thus, if −0·52° C. were to be taken as the lowest numerical value for pure milk, a sample freezing at −0·44° C. would clearly contain the same amount of solids as normal milk, but in a volume of water −0·52/0·44 of the normal amount, 8 of water to 44 of milk, an addition of 18·2 per cent of water.

With a little practice the freezing-point determination can be carried out very rapidly; four samples were examined in fifty minutes on one occasion, two of the determinations being repeated a second time. The apparatus used was the ordinary one, Raoult's, with a Beckmann thermometer. The small error in the zero, owing to the glass of the thermometer bulb not having contracted fully when determinations are made rapidly, may be avoided by determining the scale reading corresponding to the freezing-point of pure water under exactly similar conditions as to degree and time of cooling. All measurements should be made on a rising column of mercury, when the liquid freezes and rises to its true freezing-point after supercooling. The best temperature for the freezing mixture employed is −5° to −6° C., as supercooling will then occur in the milk, but not to too great an extent.

Summary.

The mean freezing-point of cow's milk is −0·55° C.; the variations from this only rarely exceed 0·03° C., above or below the mean. The freezing-point of cow's blood is −0·62° C.

The determinations of the freezing-point and specific gravity of a sample of milk are sufficient to show, on the one hand, whether it has been diluted with water, and, on the other, whether fat has been removed. The freezing-point of milk is not affected by the presence or absence of fats.

University Chemical Laboratory,
Trinity College, Dublin.

THE

PREPARATION AND BEHAVIOUR OF POLONIUM.

By F. GIESEL.

I. *Preparation of Polonium.*

As polonium is known to be a derivative of radium, radium salts, if they are old enough, must be the best and purest material for its preparation. As a matter of fact, even before I knew of this relation, I had succeeded in precipitating polonium from pure radium solutions on metallic bismuth or platinum (*Ber.*, 1903, xxxvi., 2369). Later, I obtained polonium by precipitation with sulphuretted hydrogen. The invisible precipitate is retained by filter-paper, which then shows the effects of the best polonium.

Radium mother-liquors (resulting from the crystallisation of barium radium bromide) contain other active impurities besides the decay products of radium (*Ber.*, 1902, xxxv., 3611). With sulphuretted hydrogen a distinct precipitate is obtained, consisting chiefly of lead sulphide. When this is treated with hot concentrated hydrochloric acid the polonium goes into solution. In the residual lead chloride (mixed with undecomposed sulphide) there is another active substance; it is not polonium, and possesses a constant β-radiation. Evidently the lead chloride, which was previously obtained from radium mother-liquor, and which I sent to Demarçay in 1901 for spectroscopic examination, contained the same substance (*Ber.*, 1902, xxxv., 102). Recently, I proved the absence of radium in a similar preparation much more clearly than Demarçay could with the spark spectrum, by showing that its emanation is not present. It might be supposed that Radium D was in equilibrium with Radium E and Radium F, but a piece of copper immersed in the hydrochloric acid solution showed so little α-radiation—which bore no relation to the strong β-radiation of the preparation and the Radium D it was supposed to contain—that an unknown substance with a long duration of life seems to be present. This can be proved only by a further investigation.

To prepare larger quantities of polonium, we have, as before, to fall back upon the lead from pitchblende. In the middle of 1900 I first showed (*Ber.*, 1900, xxxiii., 1667; see also the subsequent articles on Polonium) that both α- and β-radiating polonium (thus, Radium E and Radium F) can be obtained from this lead, either by dissolving the lead chloride in water and using the insoluble residue, or by extracting the lead chloride with hydrochloric acid. These two methods always seemed to me the best, especially when it is remembered that most of the polonium is carried down with the barium-radium-lead sulphate.

At the beginning of 1907 I had about 40 kilogrms. of this lead chloride at my disposal. There was, undoubtedly, a considerable amount of polonium in it because a specimen reduced to metallic lead by means of carbon made a zinc sulphide screen scintillate. Radium, which was still present in traces in the lead chloride did not go over into the regulus, as Elster and Geitel showed (*Zeit. Phys. Chem.*, 1906, vii., 841).

The working up of the product was completed in about two months. The lead chloride was first dissolved in water, freed from the small quantities of insoluble substances, and a little dilute sulphuric acid was added to remove the radium as far as possible. (The polonium was obtained from this precipitate separately). The lead solution was then precipitated with ammonia, the precipitate digested with a large excess of pure concentrated hydrochloric acid, and the acid liquid was separated from lead chloride. The lead chloride, which separated in a fine state of division, was again subjected four or five times to the same extraction with pure hydrochloric acid. All the hydrochloric acid liquors were concentrated separately, and again concentrated after the removal of the lead chloride which crystallised out.

Sulphuretted hydrogen precipitated from the first extracts some grms. of a mixture of arsenic, lead, bismuth, copper, and traces of mercury. The subsequent extracts gave smaller precipitates consisting almost entirely of copper. (Only traces of radium were present in the last two extracts). After extraction of the sulphides with ammonium sulphide the lead-bismuth-sulphide was split up by boiling with concentrated hydrochloric acid, and the bismuth was precipitated as oxychloride, while the copper was obtained almost pure as undecomposed sulphide.

It was found that in these circumstances very little polonium (but much Radium E) goes over into the bismuth, and much more very pure polonium remains behind with the copper sulphide. If the copper sulphide is decomposed by nitric acid, and the solution is saturated with ammonia, the polonium is precipitated in the form of a few hardly visible white flakes, which, when collected on a filter and dried, leave behind a thin yellowish grey deposit.

II. *Behaviour of Polonium.*

The new precipitate is more active than deposits of polonium on metals. It is specially noteworthy that it causes strong ozonisation of the air with luminescence, besides bright phosphorescence of the zinc sulphide screen. This shows clearly the great purity of the preparation, as otherwise the α-particles could not appear in quantity. The paper near the precipitate is decomposed in a few days in such a way that the deposit can easily be removed with a knife. With two or three drops of hydrochloric acid a yellow-brown solution is obtained, like platinum chloride, which becomes colourless when an oxidising agent, *e.g.*, nitric acid or hydrogen peroxide, is added. I have already noticed this colouration of solutions containing much polonium in hydrochloric acid, and regard it as an indica-

tion of the presence of a good preparation. I have not made a statement on the subject before, because the polonium itself could not cause the colouration, for then it must disappear on immersing metallic bismuth in the solution, with the removal of the polonium. My suggestion that traces of vanadium and iron were carried down could not be absolutely disproved, owing to the difficulty of analysing such small amounts of costly substances, but from the method of preparation such large quantities of impurities, especially in new preparations, are not likely to be present. I am rather of the opinion that the colouration is connected with Radium D which in all probability is contained in the polonium preparation. This is shown by the fact that after a piece of bismuth has been made active, four pieces of copper one after the other, at intervals of about one month, can be made strongly active in the same solution. The intermediate product, Radium E, must undoubtedly have caused a considerable amount of β-radiation in the solution, but no sign of it was to be detected with the Röntgen screen.

The strip of bismuth turned brown or blue in the solution, like steel when tempered; it was used by Stark and Giesel for physical investigations (*Zeit. Phys. Chem.*, 1907, viii., 580). The deposit was on both sides, 2 cm. long and 4 mm. broad, and produced between two connected metallic plates, 3·5 cm. long and 2 cm. broad, facing one another at a distance of 2·2 cm., a current of $1{\cdot}3 \times 10^{-6}$ ampères with a difference of potential of 440 volts.

On the (polished) copper foil, besides corrosion, there appeared only a light greyish white film, so slight that the colour of the copper was hardly affected by it. Platinum was absolutely unaltered, although it also showed intense activity.

No relationship to tellurium could be discovered.

No helium could be detected in two-year-old vacuum tubes containing polonium.—*Berichte*, 1908, xli., 1059).

THE FERTILISING VALUE OF SNOW.

By FRANK T. SHUTT, M.A., F.I.C.,
Chemist, Dominion Experimental Farms.

In the month of February last analyses were made of certain river ices for the purpose of determining their relative purity. The blocks of ice examined were from 18 to 22 inches in thickness, the upper or first 6 to 7 inches forming a well-marked layer characterised by a somewhat porous structure and a certain opacity. Beneath this layer the ice was perfectly hyaline. The analysis of this surface layer revealed the fact that its free ammonia was considerably higher than that of the rest of the ice, and this fact, though explained in some degree by the well-known observation that purification during freezing results, in the case of thick ice, in the lower layers being purer than those nearer the surface, suggested the presence of snow in the ice, and that this snow possessed a high ammonia content. That the snow, if present, must be *in* and not *on* the ice was assured by removing from the surface all loosely attached snow before cutting the blocks from the river.

Our search for analyses of snow in Canada was not successful; apparently no such data are on record. The writer thought therefore that a chemical examination of the snow might furnish results that would prove interesting, especially from the agricultural standpoint, since the greater part of such nitrogen compounds as the snow contains must eventually serve to fertilise the soil.

The collection of the snow samples examined was made in the Arboretum of the Central Experimental Farm, an area of 65 acres devoted to the growth of trees and shrubs. The farm, comprising about 465 acres, is situated on the confines of the city of Ottawa, between the Ottawa and Rideau Rivers, and about 3 miles south-west from the General Post Office. The atmosphere of this locality, while naturally not free from smoke, may be considered as fairly pure—for Ottawa is not a city characterised by "tall chimneys," and besides the few residences on the farm there is only a single line of a little used railroad in the immediate vicinity.

Snow had lain since November, and this examination did not commence till nearly the end of February, consequently data cannot be presented in this paper for the snow-fall of the whole season of 1906-07. With the exception of the first collection, which represents the surface 1½ inches of the accumulated snow, the samples submitted to analysis were all freshly fallen snow, care being exercised to collect either during the snow-fall or within a few hours of its cessation. The snow was allowed to melt at room temperature (about 70° F.), in a clean covered glass vessel. Not one of the samples, as taken, appeared in the slightest degree dirty or soiled, all to the eye at the time of the collection were of the purest whiteness; nevertheless, on melting there was on the surface of the resulting water or clinging to the sides of the vessel a certain amount of sooty material, and frequently also there was a slight deposit.

The determinations made comprised nitrogen present as free ammonia, albumenoid ammonia, and nitrates and nitrites.

The tabulated data are as follows:—

Nitrogen (*Parts per Million*).

Date of collection. 1907.	As free ammonia.	As albumenoid ammonia.	As nitrates and nitrites.
February 21	0·243	0·045	0·136
February 25	0·276	0·078	0·300
March 4	0·161	0·044	0·170
March 4 (twelve hours after preceding) ..	0·171	0·047	0·170
March 15	0·412	0·045	0·390
March 20	0·284	0·058	0·128
March 25	0·095	0·049	0·111
April 8..	0·140	0·058	0·024
April 10	0·255	0·058	0·107
April 17	0·589	0·066	0·317
April 25	0·360	0·041	0·033
May 4	0·082	0·033	0·065
Average	0·256	0·052	0·163

Total nitrogen (average) = 0·471 part per million.

From the wide fluctuations noticeable in the nitrogen content of these samples it is evident that the condition of the atmosphere of a locality may change both frequently and considerably, though it may also be supposed that the size of the flakes and the temperature of the atmosphere during the fall exert an influence on the filtering and solvent powers of the snow. The writer thought it quite probable that when the period since the preceding snow-fall had been a brief one, say, a day, there would be a smaller nitrogen content than when a longer period, several days or a week, ensued, but the data do not show that this was always the case. Nor did we find any marked differences in purity between samples collected at the beginning and towards the close of the same snow storm, though in this matter we can only present data from one fall, that on March 4. Next winter we hope to obtain further results on this and one or two related points.

Of the total nitrogen, that of the free ammonia constituted the greatest part, that of the albumenoid ammonia the least; the nitrogen in the form of nitrates and nitrites occupies an intermediate position. This order is not invariably maintained, and in a few instances we further notice that the nitrates and nitrites are exceptionally high.

The total snow-fall at Ottawa for the winter 1906-07 was 85·5 inches, the amount per month being as follows:—

November, 1906	.. ..	7·75 inches
December „	.. ..	21·75 „
January, 1907	.. ..	12·50 „
February, „	.. ..	17·25 „
March, „	.. ..	11·50 „
April, „	.. ..	7·25 „
May, „	.. ..	7·50 „

The average snow-fall at Ottawa from data for the past sixteen years is 90·06 inches.

To estimate the amount of nitrogen in the snow-fall per acre, it will be necessary in the first place to accept the assumption that 10 inches of snow are the equivalent of 1 inch of rain, and secondly that the present averages are representative of the whole winter's fall. Since 1 inch of rain over one acre weighs, approximately, 113 tons 600 lbs., we have had, per acre, during the winter, 968 tons 1430 lbs. of snow-water. This contained 0·471 part per million of combined nitrogen, which, by calculation, gives 0·912 lb. of nitrogen in the snow over this area. With an average fall of 90 inches and with our present averages, we could state that the winter's snow furnished, approximately, per acre, 1 lb. of nitrogen valuable as a fertiliser.

We must not suppose that the whole of the fertilising, or to speak more correctly, the agricultural value of snow lies in the nitrogen it possesses; nevertheless, we have in these data some support for the widely accepted belief that snow is a direct fertiliser. It is very evident, however, that the value of snow in this respect has been greatly over-estimated by our farmers.

The annual rainfall at Ottawa has averaged for the past sixteen years 26·56 inches, practically three-fourths of the whole precipitation. If we assume that its nitrogen content is approximately that of the snow, we have a total of about 4 lbs. of combined nitrogen furnished per acre annually from the atmosphere, an amount very similar to that found in other countries.

In concluding this preliminary note on the snow as it falls at Ottawa, it may be stated that this work, it is hoped, will be continued next winter, and that during the next summer the nitrogen content of the rain will be ascertained. The present data are interesting, but their value will be much enhanced by further results of a confirmatory character.—*Transactions of the Royal Society of Canada*, [3], i., p. 35.

SOME NEW COMPOUNDS OF INDIUM.

By F. C. MATHERS and C. G. SCHLUEDERBERG.

THIS paper describes the preparation and properties of four new compounds of indium: the perchlorate, the iodate, the selenate, and the cæsium-selenium alum.

Indium Perchlorate, $In(ClO_4)_3.8H_2O$.—Metallic indium was dissolved in dilute perchloric acid. This solution was evaporated upon a hot plate to a concentration such that when cooled in a mixture of ice and salt, small crystals were formed. The beaker was then placed in a vacuum desiccator containing concentrated sulphuric acid, where the crystallisation continued in a satisfactory manner. The crystals were rapidly rinsed with a small amount of water, dried on filter-paper, and then placed in the vacuum desiccator for a short time.

The metallic indium that was used had been deposited electrolytically, and then fused in a charcoal crucible in a current of hydrogen. This fusion was necessary to remove salts that were occluded from the electrolyte. The perchloric acid that was used was purchased from Schuckhardt. It contained a small quantity of sulphuric acid, which was removed by the addition of the proper amount of barium hydroxide.

Two different methods were used to determine the indium in the indium perchlorate. The shorter procedure consists in heating the sample to a temperature of about 200°, at which decomposition of the perchlorate takes place, then evaporating with nitric acid, and finally igniting the nitrate to the oxide. In the other method the indium is precipitated as the hydroxide with ammonium hydroxide, and is weighed as the oxide. The second method is preferable, since it permits determinations of both the indium and the chlorine (ClO_4) in the same sample. To determine the chlorine, the filtrate from the indium hydroxide was treated with an excess of sodium carbonate and a few drops of potassium permanganate. It was then evaporated to dryness on a water-bath, and heated to near fusion, this treatment decomposing the perchlorate and yielding a chloride. The mass was dissolved in dilute nitric acid, and the solution was freed from the insoluble manganese dioxide by filtration. The chlorine in the filtrate was precipitated and weighed as silver chloride.

	Theory for $In(ClO_4)_3.8H_2O$ (per cent).	Found (per cent).*			
Indium oxide .	24·92	24·82	24·73	24·83	(*a*)
Chlorine.. ..	19·08	19·05	18·67	—	

(*a*) Determined by Method 1.

Attempts to make direct determinations of the water were unsuccessful on account of decomposition and the formation of a basic salt with a loss of chlorine. Samples of the crystals that had been dried for several hours in the vacuum desiccator gave higher values for the indium oxide, 25·4 and 25·7. These values agree with the theory for $In(ClO_4)_3.7H_2O$. This is evidently due to the loss of water of crystallisation, since several different samples that were dried for only a few minutes gave results that showed eight molecules of water.

Indium perchlorate is a colourless crystalline deliquescent compound that is soluble in water and in absolute alcohol, but much less soluble in ether. It easily forms saturated solutions in water. Basic salts are precipitated from a neutral water solution when the temperature is raised to 40°. When heated in the open air, the crystals fuse at about 80°, but do not form a clear liquid. When the heating is carried to a higher temperature, but not to a red heat, the substance decomposes with a liberation of chlorine. The residue is insoluble in water, but is easily soluble in dilute nitric acid, and this solution gives a strong test for chlorine.

Indium Iodate, $In(IO_3)_3$.—Anhydrous indium trichloride was prepared and sealed off in a glass tube by a method previously described (Mathers, *Journ. Am. Chem. Soc.*, 1907, xxix., 485). Potassium iodate was re-crystallised twice from water. This sample was analysed by treating it with dilute sulphuric acid and potassium iodide, and titrating the iodine that was liberated. Taken, 0·0750 grm. KIO_3; found, 0·0749 grm.

Equivalent quantities of the indium trichloride and of potassium iodate were dissolved separately, and then mixed. A precipitate formed immediately, but it showed no crystalline structure when examined with a microscope. The entire solution was evaporated to dryness upon a water-bath, and the residue was collected upon a Gooch crucible, and was thoroughly washed with cold water. (This is the method employed in his research upon iodates by A. Ditte, *Ann. Chim. Phys.*, 1890, [6], xxi., 145). The crucible and contents were dried over sulphuric acid in a vacuum desiccator. Analyses of several samples prepared in this way did not give constant results. The substance was then dissolved in boiling nitric acid (1 : 10 by volume). On evaporation of this solution, the indium iodate separated in imperfect broken crystals whose crystal system could not be determined. These crystals were washed with water, and dried in a vacuum desiccator. The results of the analyses were as follows:—

	Theory for $In(IO_3)_3$ (per cent).	Found (per cent).	
Indium oxide..	21·71	21·76	21·93
Iodine	59·53	59·19	59·30
Water at 125° .	0·08		
Loss at 160° ..	(Decomposition, brown colour)	0·40	

The indium was precipitated as the hydroxide with ammonium hydroxide, and was weighed as the oxide. The iodine was calculated from the titration with sodium thiosulphate of the iodine that was liberated when a sample was treated with potassium iodide and dilute sulphuric acid.

Indium iodate is a white crystalline anhydrous compound. It is soluble in 1500 parts of water at 20°, and in 150 parts of 1 : 5 nitric acid at 80°. All attempts to grow large crystals from these solutions were unsuccessful. It is soluble in dilute sulphuric acid and in hydrochloric acid, but the latter causes a decomposition with the liberation of chlorine. The crystals decrepitate when heated with a free flame, become brown in colour, and give off iodine vapour. If touched with a red-hot wire they explode, and form a cloud of iodine vapour.

Indium Selenate, $In_2(SeO_4)_3.10H_2O$.—Indium selenate was prepared by dissolving indium hydroxide in selenic acid, which had been made according to the following method :—

Flue dust known to be rich in selenium was heated in a porcelain dish with a strong solution of potassium cyanide for several hours. On filtering, a clear amber-coloured solution of potassium selenocyanate, KCNSe, was obtained. A current of filtered air was passed through this solution for several hours in order to separate any tellurium that might have been dissolved with the selenium. A small quantity of a dark coloured precipitate that separated was filtered off. The filtrate was cooled to about zero degrees, and cold 50 per cent hydrochloric acid, sufficient to entirely precipitate the selenium, was added, care being taken to add the hydrochloric acid slowly to avoid an appreciable rise of temperature. The selenium is thrown down as a bright red amorphous precipitate, which was filtered off, and thoroughly washed. This was re-dissolved in a 10 per cent solution of potassium cyanide, treated with air, precipitated in the cold as before, filtered off, washed very thoroughly, and dried.

The selenium was then dissolved in concentrated nitric acid, and the solution evaporated to dryness on the water-bath, re-dissolved in very dilute hydrochloric acid, and again evaporated to dryness. The selenium dioxide thus obtained was dissolved in a little water, and added to chlorine water, through which a stream of chlorine was allowed to bubble, thus oxidising the selenium dioxide to selenic acid. After being thus treated for several hours with chlorine the liquid was freed as far as possible from excess of that gas by passing through it a current of air.

The solution of selenic acid was neutralised with copper carbonate and freshly precipitated copper hydroxide. The blue solution of copper selenate thus obtained was filtered, concentrated on the water-bath, and set aside to crystallise. Blue triclinic crystals of copper selenate separated. These were re-crystallised from water solution, and again dissolved in water, and the solution freed from copper by electrolysing in a platinum dish at low current density (R. Metzner, *Comptes Rendus*, 1898, cxxvii., 54). Electrolysis was continued until no test for copper could be obtained with either ammonium hydroxide, potassium sulphocyanate, or potassium ferrocyanide in small portions of the solution. The solution of pure selenic acid thus obtained was treated with indium hydroxide. Indium selenate crystallised out in white, easily soluble, hygroscopic crystals. Analysis gave the following results :—

	Theory for $In_2(SeO_4)_3.10H_2O$ (per cent).	Found (per cent).
Indium oxide ..	33·08	32·9—33·0
Selenium	28·30	28·3—28·2

Indium Cæsium Selenate, $CsIn(SeO_4)_2.12H_2O$.—Cæsium-indium-selenate, the alum, was made by crystallising a solution of cæsium selenate (prepared from cæsium hydroxide and selenic acid) and indium selenate.

The alum crystallises in beautiful colourless octahedra, belonging to the tetragonal system, which are soluble in water, efflorescent in the air, and are of the following composition :—

	Theory for $CsIn(SeO_4)_2.12H_2O$ (per cent).	Found (per cent).
Selenium	21·18	21·04
Indium	15·3	15·5
Cæsium	17·7	17·8

In the above analyses the selenium was determined by repeated precipitation with sulphur dioxide gas from a hot dilute solution of the salt. The precipitate was collected on a Gooch filter, and the filtrate was boiled down, and again treated with sulphur dioxide. It was found necessary to repeat this operation several times in order to remove all of the selenium from the solution. The Gooch filter was dried at 102—105°, and the selenium was weighed.

The indium was precipitated by ammonium hydroxide as the hydroxide from the hydrochloric acid solution of the salt, collected on an ashless filter, heated in a porcelain crucible, and weighed as In_2O_3.

For the determination of the cæsium, the selenium was first removed, and the cæsium was then precipitated from the chloride solution by chlorplatinic acid, and weighed as cæsium chlorplatinate.—*Journal of the American Chemical Society*, xxx., No. 2.

THE DETERMINATION OF VANADIC AND MOLYBDIC ACIDS IN THE PRESENCE OF ONE ANOTHER.

By GRAHAM EDGAR.

A METHOD has been recently proposed by Glasmann (*Ber.*, xxxviii., 600) for the estimation of vanadic and molybdic acids in the presence of one another, based on the different reducing action of zinc and magnesium upon the hydrochloric acid solution of these acids. In a previous paper from the Kent Chemical Laboratory of Yale University (Gooch and Edgar, *Am. Journ. Sci.*, xxv., 233) it has been shown that the action of magnesium is irregular, and not adapted to an accurate quantitative method. Vanadic acid, however, is reduced to the state of dioxide by a column of amalgamated zinc, and may be estimated by titration with potassium permanganate, if the receiver be charged with a solution of ferric alum to anticipate the oxidising action of the air (Gooch and Edgar, *loc. cit.*). That molybdic acid is under the same conditions reduced to the state of Mo_2O_3 has been shown by Dudley (unpublished, but privately communicated by Prof. Henry Fay), and, independently, by Randall (*Am. Journ. Sci.*, xxiv., Oct., 1907). The ease with which vanadic acid is reduced to the state of tetroxide by sulphur dioxide, and the difficulty, as has been found, with which this reagent attacks molybdic acid under proper conditions of acidity and concentration, suggest its use in one of two processes of differential action for the determination of these acids. To determine the conditions under which molybdic acid is unaffected by sulphur dioxide, a series of experiments was made in which solutions of molybdic acid of varying concentrations, acidified with varying amounts of sulphuric acid, were heated to boiling, and treated with a current of sulphur dioxide for varying lengths of time. The excess of sulphur dioxide was then removed by boiling the solution, a current of carbon dioxide being meanwhile passed into it, and the degree of reduction was determined by titration with nearly N/10 potassium permanganate. The solution of molybdic acid was standardised by the method of Randall (*loc. cit.*), and by evaporating a portion to dryness, and igniting at low red heat. The results of the experiments are given in Table I.

The results show that if the concentration be not greater than 0·2 grm. of MoO_3 in 50 cc. of solution, and the acidity not less than 1 cc. of sulphuric acid (sp. gr. 1·84) in the same volume, the molybdic acid is not reduced, and that if the acidity be increased to 5 cc. of sulphuric acid, reduction does not occur at even a concentration of 0·4 grm. in 25 cc.

TABLE I.

Volume of solution.	MoO_3.	H_2SO_4 (sp. gr. 1·84).	Time of treatment with SO_2.	$KMnO_4$ N/10 × 1·004.	Colour of solution.
Cc.	Grm.	Cc.	Mins.	Cc.	
25·0	0·200	Faintly acid	10	0·15	Light blue.
35·0	0·200	0·5	10	0·5	Faint blue.
50·0	0·200	1·0	10	—	Colourless.
75·0	0·200	2·0	10	—	,,
50·0	0·200	2·0	30	—	,,
25·0	0·200	5·0	10	—	,,
25·0	0·400	5·0	10	—	,,
50·0	0·400	5·0	10	—	,,
50·0	0·400	10·0	10	—	,,
50·0	0·400	15·0	10	—	,,

TABLE II.

Ferric alum (10 per cent).	Phosphoric acid syrup.	$KMnO_4$ N/10 × 1·052.	$KMnO_4$ N/10 × 1·052	V_2O_5 taken as $NaVO_3$.	MoO_3 taken as $(NH_4)_2MoO_4$	V_2O_5 found.	MoO_3 found.	Error on V_2O_5.	Error on MoO_3.
Cc.	Cc.	Cc.	Cc.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
50	8	11·95	74·15	0·1144	0·1930	0·1146	0·1934	+0·0002	+0·0004
50	8	11·95	74·00	0·1144	0·1930	0·1146	0·1926	+0·0002	−0·0004
50	8	11·94	74·20	0·1144	0·1930	0·1145	0·1936	+0·0001	+0·0006
25	4	5·97	37·10	0·0572	0·0965	0·0572	0·0965	—	—
25	4	5·97	37·05	0·0572	0·0965	0·0572	0·0962	—	−0·0003
25	4	5·98	37·12	0·0572	0·0965	0·0573	0·0963	+0·0001	−0·0002
35	6	11·95	55·0	0·1144	0·0965	0·1146	0·0967	+0·0002	+0·0002
35	6	11·95	55·0	0·1144	0·0965	0·1146	0·0967	+0·0002	+0·0002
35	6	11·96	54·86	0·1144	0·0965	0·1147	0·0958	+0·0003	−0·0007
65	10	17·92	92·0	0·1716	0·1930	0·1719	0·1931	+0·0003	+0·0001
65	10	17·94	92·05	0·1716	0·1930	0·1720	0·1931	+0·0004	+0·0001
65	10	17·92	92·02	0·1716	0·1930	0·1719	0·1932	+0·0003	+0·0002

A series of experiments was then made in which solutions containing vanadic and molybdic acids were diluted to 75 cc., acidified with 2 to 3 cc. of strong sulphuric acid, heated to boiling, and subjected to a current of sulphur dioxide for a few minutes until the clear blue colour indicated the complete reduction of the vanadic acid to the state of tetroxide. The boiling was continued for some time, a current of carbon dioxide being passed into the liquid until the last traces of sulphur dioxide had been removed. Titration was then effected by nearly N/10 potassium permanganate, and the vanadic acid was calculated from the equation,—

$$5V_2O_4 + 2KMnO_4 + 3H_2SO_4 = 5V_2O_5 + K_2SO_4 + MnSO_4 + 3H_2O.$$

The solution, preceded by 100 cc. hot water and 125 cc. of dilute (2½ per cent) sulphuric acid, and followed by 100 cc. dilute sulphuric acid, and 200 cc. of hot water, was passed slowly through a column of amalgamated zinc in a Jones reductor ("The Chemical Analysis of Iron," Blair, p. 225), the receiver containing a solution of ferric alum. The hot solution was then titrated with nearly N/10 potassium permanganate, a little phosphoric acid being added to decolorise the ferric salt.

Since the reduction of vanadic acid is in this case to the condition of dioxide, V_2O_2, if the number of centimetres of permanganate used in the titration of the tetroxide be multiplied by three and the product subtracted from the total number of centimetres of permanganate used in the final titration, the result is the number of centimetres used in oxidising Mo_2O_3 to MoO_3, from which the amount of molybdic acid present may be easily calculated. The results, given in Table II., show that molybdic acid and vanadic acid may be accurately estimated in the presence of one another by two processes of reduction and oxidation, the reduction being made first by sulphur dioxide and last by amalgamated zinc.

In conclusion, the author desires to thank Prof. F. A. Gooch for many kind and helpful suggestions and criticisms during the progress of the work.—*American Journal of Science*, xxv., p. 332.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 2nd, 1908.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

(Concluded from p. 237).

81. "*The Hydrolysis of Amygdalin by Emulsin.*" Part I. By SAMUEL JAMES MANSON AULD.

By means of specially devised apparatus, the hydrolysis of amygdalin by emulsin has been studied in detail by estimating the hydrocyanic acid produced during the reaction. It has been shown that Jorissen and Hairs' "emulsin" is really a mixture of two enzymes, namely, true emulsin and a maltase-like ferment. The effect of varying the concentration of amygdalin and emulsin has been investigated, as also the action of many inhibitants. Of particular importance is the fact elucidated that the activity of emulsin is intimately bound up with basic and acidic groups, as both acids and alkalis only render the ferment inactive and do not destroy it except in high concentrations. Contrary to the statements of Tammann, the decomposition of amygdalin by emulsin nearly approaches completion, as much as 97 per cent of the available glucoside being decomposed as measured by the hydrocyanic acid formed. The end-point of the reaction has been found to be independent of the temperature, and the temperature-coefficients of the action have been measured over a range of 45°.

82. "*Complex Nitrites containing Potassium and Lead.*" (Preliminary Note). By ANDREW NORMAN MELDRUM.

The reaction between potassium nitrite and a lead salt (which may be the acetate, nitrate, chloride, bromide, or iodide) results in the production of complex-compounds, which, in addition to potassium, lead, nitrosyl, and water, may contain one or more equivalents of the negative ion with which the lead was originally associated. The

products vary in colour from bright yellow to orange, and they contain potassium and lead, as a rule, in the atomic ratio of 3 : 2.

In attempting to prepare the compound $K_2Pb(NO_2)_2,(NO_3)_2,H_2O$, $(KO,NO_3,PbO,NO_5 + HO$ (Hayes, *Quart. Journ. Chem. Soc.*, 1860, xiii., 335), the author finds that the product has always the composition, approximately, if not exactly, $K_2Pb(NO_2)_3NO_3,H_2O$.

Metallic lead is more easily attacked by solution of lead nitrate to which potassium nitrate has been added than by lead nitrate solution alone.

83. "*The Composition and Formula of Wells' Potassium Lead Periodide.*" By Andrew Norman Meldrum.

A potassium lead periodide has been described by Wells (*Am. Journ. Sci.*, 1893, xlvi., 190), who assigned to it the formula $K_3Pb_2I_8,4H_2O$, analogous to that of the perbromide, $K_3Pb_2Br_8,4H_2O$, described in the same paper. Actually, the analyses of six different preparations of the substance were in good agreement with one another, and with the formula $K_9Pb_4I_{19},10H_2O$. In arriving at the formula $K_3Pb_2I_8,4H_2O$, Wells made the assumption that the material analysed was "contaminated with about 16·5 per cent of potassium iodide, and that an excess of water was present, possibly on account of the hygroscopic properties of that salt."

Potassium iodide (150 grms.), lead iodide (4 grms.), iodine (70 grms.), and water (90 cc.) were mixed, and the mixture was slowly heated to the boiling-point and filtered to remove any undissolved lead iodide. After some time, crystals separated, which were collected, drained on a porous tile, and exposed to the air until the odour of iodine was very faint. The product consisted of shining *violet* prisms, not unlike potassium permanganate, and hardly corresponded with Wells' "brilliant *black*, prismatic crystals."

The substance was analysed by methods different from those used by Wells. The lead and potassium were determined together as the sulphates, and the lead separately as chromate. Thiosulphate solution was used to determine (1) the total iodine (after addition of sulphuric acid and ferric alum, with subsequent distillation), and (2) the "extra" iodine. Water and "extra" iodine were determined together as loss on heating at 100°.

Found : mixed sulphates = 53·14, 52·97 ; Pb = 21·71, 21·67 ; total iodine = 64·19 ; "extra" iodine = 6·76, 6·81 ; loss at 100° = 11·33, 11·04.

$K_9Pb_4I_{19},10H_2O$ requires mixed sulphates = 52·97 ; Pb = 21·95 ; total iodine = 63·96 ; "extra" iodine = 6·74 ; loss at 100° = 11·52 per cent.

Potassium iodide, if present in a mixture to the extent of 16·5 per cent, the assumption which Wells makes, would surely be visible to the naked eye, but the material which the author analysed, when examined under the microscope, had all the appearance of a single substance, and it was not hygroscopic. The formula of the periodide is therefore $K_9Pb_4I_{19},10H_2O$, and it is probable that Wells, in assigning similar formulæ to the perbromide and the periodide, was led astray by the desire for uniformity.

84. "*The Molecular Complexity of Amides in various Solvents.*" By Andrew Norman Meldrum and William Ernest Stephen Turner.

The authors have determined the molecular complexity by the boiling-point method of eleven amides, namely, benzamide, salicylamide, acetanilide, benzanilide, acetamide, monochloroacetamide, dichloroacetamide, trichloroacetamide, trichlorolactamide, carbamide, and malonamide in six solvents, so far as the solubility of the amides would allow (compare *Proc.*, 1907, xxiii., 165). The Lumsden-Walker apparatus was employed, and the boiling-points were specially corrected for the mere pressure effect of the accumulation of liquid in the boiling tube. The following table summarises the results, and includes also the dielectric constants of the solvents :—

A. Number of amides investigated.
B. Number of amides which form simple molecules.
C. Number of amides which form associated molecules.
D. Dielectric constant of solvent.

Solvent.	A.	B.	C.	D.
Benzene . .	8	1 doubtful	7	2·3 at 18°
Ether	5	1	4	4·4 at 18°
Chloroform . .	9	2	7	5 at 22°
Acetone . .	10	9	1	25 at 20°
Alcohol . .	11	9	2 doubtful	26 at 20°
Water	9	4 and 1 doubtful	4	80 at 17°

Except in the case of water, these results are in good accordance with the Nernst-Thomson theory that the smaller the dielectric constant of the solvent the greater is the association of the solute. Association in ether tends to be less than in benzene and much the same as in chloroform, just as would be inferred from the dielectric constant. Ether has hitherto been regarded as a non-associating solvent. In investigations into the physical properties of the amides and allied compounds, the most suitable solvent is alcohol, in which association is at a minimum.

Benzamide, salicylamide, acetanilide, and dichloroacetamide, the only instances of the kind known to the authors, have a greater molecular complexity in water than in alcohol. This is quite contrary to what would be expected from the Nernst-Thomson theory.

85. "*The Optical Activity of Compounds having Simple Molecular Structure.*" By William Jackson Pope and John Read.

The authors described crystalline salts formed by chlorosulphoacetic acid and chlorobromomethanesulphonic acid with the optically active alkaloids, strychnine and quinidine. The two acids each contain an asymmetric carbon atom in the molecule, but, although their strychnine and quinidine salts crystallise well, no evidence was obtained that the acids are resolvable into enantiomorphously related components.

86. "*Acetylketen : a Polymeride of Keten.*" By Frances Chick and Norman Thomas Mortimer Wilsmore.

It has been shown (*Nature*, 1907, lxxv., 510 ; *Trans.*, 1907, xci., 1938) that keten, both in the liquid and the gaseous states, condenses at the ordinary temperature to form a pungent-smelling, brown liquid. The latter has now been further studied. On distillation, a colourless liquid passes over, leaving a brown, non-volatile residue. This liquid boils at 126—127°, and solidifies in a freezing mixture to a white solid, which melts at −7° to −6°. It has an extremely pungent smell, suggestive both of acetic anhydride and of acrolein. On standing, even in absence of air, it slowly turns brown. Analysis gave C = 56·9, H = 5·0, whilst the depression of the freezing-point of benzene and the vapour density, determined by Gay Lussac's method, agreed in giving a molecular weight of nearly 85, showing that the substance has the composition $C_4H_4O_2$, which requires C = 57·1 ; H = 4·8 per cent M.W. = 84.

The liquid dissolves slowly in water, forming a strongly acid solution, which gives a violet colour with ferric chloride ; on boiling the aqueous solution, carbon dioxide and acetone (recognised by the iodoform, benzaldehyde, and alkaline mercuric chloride reactions) are formed, and the solution becomes neutral. Hydrogen chloride facilitates the dissolution and decomposition. On boiling the substance with aqueous alkalis, acetates are formed, hence the substance combines with water to form acetoacetic acid. It reacts vigorously with aniline, forming acetoacetanilide melting at 84°.

The new substance is therefore *acetylketen*, having the formula $CH_3{\cdot}CO{\cdot}CH : CO$ or $CH_2 : C(OH){\cdot}CH : CO$.

It reacts with two molecular proportions of phenylhydrazine, forming the colourless *phenylhydrazonephenylhydrazide*, which melts at 152—153°.

87. "*Saponification of Ethyl Formate by Water in presence of Acids as Catalytic Agents.*" By Arthur Lapworth.

Some statements in a recent paper by Stieglitz (*Am. Chem. Journ.*, 1908, xxxix., 402) have led the author to re-examine a suspicion, which he had some reason to entertain some six years ago, but which he did not then succeed in fully confirming. In recent experiments the velocity of saponification of ethyl formate in acetone solution has been measured, hydrogen chloride being used as catalyst, and the water being present in quantity small enough to be comparable with that of the ester.

Set I.—A = 10 cc. ethyl formate, 2 cc. water, made up with acetone to 50 cc. B = 10 cc. ethyl formate, 5 cc. water, made up with acetone to 50 cc.

Titre of 5 *cc.*

t = Hrs.	Mins.	A = Cc.	B = Cc.
0	0	(4·8)	(4·8)
0	4	6·1	6·55
0	10	7·5	7·4
0	27	10·45	9·75
0	59	16·35	15·2
2	58	36·3 ?	28·50 ?
6	28	41·40	42·4
22	30	43·2	57·0

Set II.—C = 10 cc. ethyl formate, 5 cc. water, made up with acetone to 50 cc. D = 10 cc. ethyl formate, 10 cc. water, made up with acetone to 50 cc.

Titre of 5 *cc.*

t = Hrs.	Mins.	C = Cc.	D = Cc.
0	0	(2·5)	(2·5)
0	1	2·7	2·5
0	6	3·3	3·0
0	29	5·85	5·75
2	0	16·05	15·8
9	18	51·0	48·9
21	9	62·6	72·5

Set III.—E = 5 cc. ethyl formate, 5 cc. water, made up with acetone to 50 cc. F = 10 cc. ethyl formate, 5 cc. water, made up with acetone to 50 cc.

Titre of 5 *cc.*

t = Hrs.	Mins.	E = Cc.	F = Cc.
0	0	(4·0)	(4·0)
0	2	4·15	4·4
0	25	6·7	8·45
0	54	9·65	15·10
1	5	11·1	17·95
1	31	14·4	25·45
6	20	32·8	58·7
18	50	42·8	65·1

The alkali used was about N/10, but was somewhat stronger in the case of Set I. The numbers in parentheses indicate about the amount of each titre due to hydrochloric acid used as catalyst in each set.

The results show clearly enough that, in the circumstances specified, the velocity of saponification is nearly independent of the concentration of the water present during a considerable part of the change, but that, when the mixture approaches equilibrium conditions, divergence is noticed for the first time.

Stieglitz has shown (*loc. cit.*, p. 417) that his own theory leads to the expression—

$$\frac{dx}{dt} = K \times k \times C_{ester} \times C_H \times [C_H \times C_{OH}]$$

or—

$$= \text{proportional to } C_{ester} \times C_H^{\infty} \times C_{water},$$

and is therefore incorrect.

This chemist is also incorrect in asserting that the author's own theory (Mellor, "Chemical Studies and Dynamics," p. 289) fails to account for the catalysis of esters by hydrogen ions; it remains the only theory in accordance with the facts, in spite of Stieglitz's remarks on the velocity of "salt formation" (*loc. cit.*, p. 425). It accounts for the dependence of the equilibrium condition on the concentration of the water, and the independence of the initial velocity of hydrolysis on that factor.

The author intends to continue with his colleague the above work, and to study the influence of the concentration of alcohol and carboxylic acid on the velocity of esterification, as well as a number of analogous cases in which the influence of the substance generally used as solvent is not fully understood.

88. "*The Triazo-group.* Part III. *Bistriazo-Derivatives of Ethane and of Acetic Ester.*" By Martin Onslow Forster, Hans Eduard Fierz, and Walter Philip Joshua.

1 : 2-*Bistriazoethane*, $N_3 \cdot CH_2 \cdot CH_2 \cdot N_3$, prepared from ethylene dichloride and sodium azide, is a colourless, refractive liquid which boils at 53° under 9 mm. pressure, and has sp. gr. 1·178 compared with water at 19°; the odour resembles that of chloroform, and the vapour is explosive. Stannous chloride liberates two-thirds of the nitrogen, giving ethylenediamine; alcoholic alkali does not set free nitrogen, but slowly eliminates hydrazoic acid.

The *compound*, $C_{14}H_{16}N_6$, which probably has the constitution $C_6H_5 \cdot NH \cdot N : N \cdot CH_2 \cdot CH_2 \cdot N : N \cdot NH \cdot C_6H_5$, arises by the action of magnesium phenyl bromide on 1 : 2-bistriazoethane, and crystallises from petroleum in lustrous, square plates with brown tinge; it melts at 128°, evolving gas with vigour. Dilute mineral acids liberate two-thirds of the nitrogen, producing aniline.

Bistriazoacetic ester, $CH(N_3)_2 \cdot CO_2 \cdot C_2H_5$, produced from dichloroacetic ester and sodium azide, is a colourless liquid which boils at 70—72° under 2 mm. pressure, and has sp. gr. 1·222 compared with water at 18°; the odour is scarcely perceptible. The ester is highly explosive, and liberates nitrogen explosively when treated with sulphuric acid. Hydrazoic acid is eliminated by alcoholic ammonia, consequently bistriazoacetamide could not be obtained.

PHYSICAL SOCIETY.

Ordinary Meeting, May 8th, 1908.

Dr. Charles Chree, F.R.S., President, in the Chair.

A paper on "*A Modified Theory of Gravitation*" was read by Dr. C. V. Burton.

If we are to regard gravitational attraction as exerted through the medium of the ether, it appears to the author difficult to avoid the conclusion that the very great (or possibly infinite) velocity with which such attractions are propagated is due to the very great (or complete) incompressibility of the ether. This conception is embodied in the pulsatory theories of Hicks, and of subsequent writers; the chief outstanding difficulty has lain in providing for that agreement of phase which must be assumed to subsist amongst the centres of pulsatory disturbance associated with the mutually attracting masses. This difficulty is avoided if we suppose that primary waves of compressional-rarefactional type are being propagated through the ether with a velocity enormously transcending that of light. These primary waves may be travelling in directions indifferently distributed, or predominantly or exclusively in one direction; but an essential point is that all effective wave-lengths should be very great, measured even by astronomical standards. Thus the pressure-changes will be sensibly in the same phase over considerable regions, and if the etherial compressibility is locally increased (or diminished) by the presence of electrically neutral matter, every particle of such matter will act as a centre of pulsatory motion.

For the electron, so far as concerns this modification of etherial compressibility, a specification is assumed which involves no restraint on the free mobility of the electron through the ether. Incidentally the dynamics of the problem assumes a relatively simple form, and a value which could be quite insignificant attaches to a "gravitational (or non-electromagnetic) term" appearing in the expression for the total inertia of an electron.

It has to be shown that, in its primary aspect, the assumed wave-motion would give rise to no observable effects. This, in fact, follows from the assumptions made, and it is only through the feeble secondary effect of gravitation that any evidence of the wave-motion could be obtained.

In attempting to work out the theory on a numerical basis, values have to be found for a considerable number of physical quantities, several of these requiring to be independently conjectured, before the remaining quantities can be determined. But the range of the values which could be reasonably assumed is a good deal more restricted than might be supposed. The author gives a plausible set of values for these physical constants.

Mr. C. S. WHITEHEAD asked if the amount of energy stored in the ether was greater or less than it was in the past.

Prof. C. H. LEES asked if the ether considered was the old one or a new one. He referred to an interesting point in the author's representation of gravitation, namely, that matter was produced by the absence of something from the ether. In the theory advocated by Osborne Reynolds matter was produced by a deficiency in the normal piling, and recent theories seek to explain matter and gravitation by the absence of something which is present in free ether.

Dr. C. V. BURTON, in reply to Mr. Whitehead, said he was not aware whether the amount of energy in the ether varied with time or not.

A paper on "*An Examination of the Formulæ for the Grading of Cables*" was read by Mr. C. S. WHITEHEAD.

In the *Journal of the Institution of Electrical Engineers* both Mr. O'Gorman and Dr. Russell have shown that it would be advantageous if cables for electric lighting were constructed so that the component of the electric intensity along a radius (in cylindrical co-ordinates) was kept constant for all points in the dielectric in the same plane perpendicular to the axis. They both find that to attain this object λr ought to be kept constant if the current is alternating, and σ/r constant if the current is steady, where λ is the specific inductive capacity, σ the specific resistance, and r the distance from the axis. In this paper the question is regarded from a much more general point of view.

Maxwell's two curl relations are taken in cylindrical co-ordinates, and it is supposed, as is quite legitimate, that the electrical and magnetic quantities are symmetrical round the axis, and that they vary as $e^{i(mz+pt)}$. We can then solve the equation, and from the continuity of the tangential components of the electric and magnetic forces obtain an equation to find m.

If P is the component of the electric intensity along a radius, β the component of the magnetic force perpendicular to a radius in a plane perpendicular to the axis, we find—

$$P = -\frac{im}{\frac{4\pi}{\sigma} + \frac{\lambda i p}{c^2}}$$

where c is the ratio of the electrostatic to the electromagnetic unit of electrical quantity. Also if I be the total current in the wire parallel to the axis, and we neglect the displacement-current in the wire in comparison with I, we have—

$$\beta = \frac{2I}{r}.$$

Putting $m = -a+ib$, it is found that $\sqrt{a^2+b^2} = \sqrt{\lambda}.h$, where h involves no quantities which have reference to the dielectric. Taking the real parts and putting P_0 and I_0 for the factors of P and I which are independent of the trigonometrical factor, we obtain—

$$P_0 = 2I_0 e^{-bz} \frac{c^2}{\lambda r} \sqrt{\frac{a^2+b^2}{p^2 + \left(\frac{4\pi c^2}{\lambda\sigma}\right)^2}}.$$

If we suppose I_0, a, b to be constants of the cable which do not vary as we vary λ or σ, we get the rules given by Mr. O'Gorman and Dr. Russell. Thus, let σ be very great, then to keep P_0 constant we must make λr constant, but if $p = 0$, that is for steady currents, we must make σ/r constant. We have seen, however, that $\sqrt{a^2+b^2}$ varies as $\sqrt{\lambda}$, so that in the case of σ very great this process suggests the rule make $r\sqrt{\lambda}$ constant. When $p = 0$ it is shown that $a = 0$ and that b varies inversely as $\sqrt{\sigma}$, so that this case suggests the rule make $\sqrt{\sigma}/r$ constant. The equation for P_0 is, however, strictly true.

Dr. A. RUSSELL complimented the author on his interesting paper and on the skill with which he had handled the mathematical equations. The question of the grading of cables was one of great importance to the electrical engineer, and it was necessary to attack it both from the mathematical and the experimental side. The author took the case of an infinitely long concentric main, and assumed that the amplitude of the current remained constant. In the practical problem the main is of finite length and the amplitude of the applied voltage is constant. The mathematical difficulties in the way of getting a complete solution were great, and so he hoped the author would continue his investigations further. Dr. Russell exhibited a portion of a Jona graded cable which had successfully withstood a testing-pressure of 150 kilovolts applied between the core and the lead sheath. If the dielectric had been air a disruptive discharge would have ensued at 23 kilovolts.

A paper entitled "*Illustrations of Geometrical Optics*" was read by Mr. R. M. ARCHER.

The principles of geometrical optics are frequently illustrated by experiments in which the images of narrow obstacles are obscured by similar obstacles arranged in the line of vision. This method is tedious, and is open to the objection that the path of a shadow is traced rather than that of a beam. The author's method is free from these objections. Light from a narrow rectilinear source is allowed to pass through a slit and fall upon a flat white surface at almost grazing incidence. It is easy to obtain upon the surface a long narrow streak of light with sharp edges; and if a mirror be placed with its plane approximately normal to the surface, another streak corresponding to the reflected ray can be seen. Similarly, the path of the beam after its emergence from a glass block or prism may be traced. Interesting effects can be obtained by using many slits and casting the beam from a distant optical lantern upon them. This mode of illumination is useful in demonstrating the formation of caustics. Quantitative results can be obtained comparable in accuracy with those given by an ordinary optical bench.

The author exhibited a series of slides illustrating various cases of reflection and refraction, and showed also several experiments with the apparatus described in the paper.

Prof. C. H. LEES expressed his interest in the neatness of the experiments, and said the author's method of dividing up a beam was a very useful one.

Mr. A. CAMPBELL congratulated the author, and remarked that the methods described could be applied to other optical experiments. In using a vibration galvanometer or an oscillograph, an easy way to obtain a curve of the wave-form was to put obliquely in the path of the beam a sheet of white paper and vibrate it.

Dr. W. H. ECCLES also congratulated the author upon his paper.

NOTICES OF BOOKS.

The Spectroscope. By T. Thorne Baker, F.C.S., F.R.P.S. London: Baillière, Tindall, and Cox. 1907.

Students of advanced chemistry have undoubtedly felt the want of a text-book on spectrum analysis which explains the use of the spectroscope in analytical work sufficiently fully for all practical purposes, and serves as an introduction to the use of the larger treatises. This want is supplied by this book, which is admirably suited for chemical students with the usual elementary knowledge of physics. The general descriptions of different types of instrument explain their construction and give indications as to the reliability and cost of some of them, and notes on methods of carrying out determinations are also added. These might with advantage be somewhat fuller, though it must be remembered that the use of the spectroscope can only be explained really satisfactorily by a competent teacher to students who have every opportunity of handling and adjusting the instrument themselves. Spectrography is fully treated, and the formulæ for the development of different plates, which in the author's own experiments have been found to be trustworthy, are of special value.

Iron and Steel. By J. H. Stansbie, B.Sc. (Lond.), F.I.C. London: Archibald Constable and Co., Ltd. 1907.

In this book is given a short general review of methods of extracting iron from its ores and of the manufacture of steel, and the reader will be able to learn from it the outlines of every step in the processes, from the preparation of the ore to the treatment of masses of iron and steel necessary to enable the engineer to make use of the metal. A short introduction deals with the elements of chemical theory, but this is so sketchy that, except to the reader who has had some opportunity of previously studying the subject, it is more likely to be confusing than helpful. In the course of the text there is a short explanation of the application of the phase rule to problems in iron and steel chemistry, and this difficult subject is made very clear. The chapter on electric smelting gives an outline of the method of employing the energy of an electric current in these industries. The book is based upon notes used by the author for courses of lectures, and should be specially valuable for technical students to amplify and possibly add interest to their lecture work.

Kurzes Lehrbuch der Organischen Chemie. ("Short Text Book of Organic Chemistry"). By William A. Noyes. Translated into German by Walter Ostwald. Leipzig: Akademische Verlagsgesellschaft. 1907.

The American edition of this book showed great originality in many respects, and beginners have found that it has done much to smooth the path of their early studies in organic chemistry. Unless the student has much more time than is usually possible to spend on his elementary course, he is apt to be somewhat appalled by the mass of material which is put before him, and which appears to make such great demands upon his memory. Later in his work he finds that what appeared isolated facts and phenomena are really only illustrations of general reactions, and order is soon evolved from chaotic disorder in his mind. The author of the text-book, of which this is an excellent translation into German, conceived the plan of reversing the usual arrangement, and of putting before the beginner general reactions first, the individual substances being studied as illustrations of the previously learnt general methods of preparation and transformation. At the end of each chapter suggestions are given for suitable laboratory work in connection with the subject of the chapter. The book is prefaced by an appreciative introduction by Prof. Wilhelm Ostwald, in which he points out its special features, and recommends it as giving a thoroughly logical presentation of elementary organic chemistry.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 13, March 30, 1908.

Phenomena in the Spark Spectrum of Yttrium attributable to Positive Electrons.—Jean Becquerel.—The author has investigated whether the rare earths which, at a low temperature, exhibit phenomena attributable to positive electrons show the same effects at high temperatures. He has detected these phenomena in the spark spectrum of yttrium. In a magnetic field the light emitted parallel to the lines of force traverses a quarter wave plate, followed by a rhombohedron placed in front of the slit of a spectroscope, so that the spectra of two inverse circular vibrations can be observed simultaneously. In these conditions the isolated rays of the rare earths give the Zeeman effect in the usual direction with more or less intensity, but with yttrium two groups of rays do not resemble the isolated rays. These rays, which are situated in the orange, have been observed by Thalén, who regards them as characteristic of yttrium. They have also been studied by Urbain. In a spectroscope of feeble dispersion they appear as flutings, but with a grating a series of asymmetric rays appears, each possessing a sharp edge towards the violet, and a more indistinct edge, followed by a diminishing light towards the other side. They follow one another regularly at intervals of 1·6 to 1·8 $\mu\mu$, increasing slightly with the wave-length, and their intensity decreases as the wave-length increases. The most marked rays have wave-length 597·05 $\mu\mu$ and 613·10 $\mu\mu$, and they form two groups. Those of the second group give the Zeeman effect in the usual direction, while those of the first exhibit the phenomenon in the opposite direction. In each group the difference of the number of vibrations between two consecutive rays is constant. It seems possible that the positive electrons which cannot be separated from the atoms, either in electric discharges nor in radio-active phenomena, and which appear strongly bound to the atoms, can, nevertheless, acquire a sufficient degree of liberty to manifest themselves in optical phenomena.

Trichlorophenol, OH(1)Cl(2.4.6) and its Transformation into Chlorinated Quinones.—E. Léger.—It is most convenient to prepare this compound by the action of a commercial solution of sodium hypochlorite (Eau de Javel) upon phenol. When fuming nitric acid acts upon it in the cold the 2.6 dichloroquinone is obtained. If a small quantity of hydrochloric acid is added to the nitric acid a mixture of trichloroquinone and tetrachloroquinone is formed. These can be separated by fractional crystallisation with alcohol.

Styrolene Oxide.—MM. Tiffeneau and Fourneau.—This oxide can be prepared by the action of powdered caustic potash on an ethereal solution of styrolene iodohydrine in the cold. In its reactions sometimes it behaves normally, binary compounds being added symmetrically, and the chain being opened as follows:—$C_6H_5—\underset{|}{CH}—CH_2—O—$, and sometimes it behaves like the isomeric phenyl acetic aldehyde, $C_6H_5—CH_2—CHO$. It is impossible to decide whether this aldehyde is formed as an intermediate product, or whether after the migration of the hydrogen the binary compound adds itself on before this aldehyde is formed, *i.e.*, to the residue, $C_6H_5—CH_2—CH<^{O--}$.

β-αα-Dialcoholated Ketone Alcohols.—E. E. Blaise and I. Herman.—The action of alkalis on oxypseudobutylethyl ketone gives a ketone containing C_7. This is identical with methovinylisopropylketone, $CH_3>C—CO—CH<^{CH_3}_{CH_3}$. The formation of this compound is apparently due to a molecular transformation, dehydration first occurring, and then migration of a methyl group.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xli., No. 6, 1908.

Osmium.—O. Makowka.—When a solution of acetylene saturated with acetone is added to an osmium solution colloid osmium is at once formed, and may be separated by heating the solution in a closed tube to 100—110°. The residue, which contains metallic osmium, may readily be filtered off, and the separation is quantitative.

Formation of Hydrogen Peroxide.—Franz Fischer and O. Ringe.—Hydrogen peroxide is formed under the same conditions as ozone, if care is taken not to keep the substance when once formed for any length of time at a temperature at which its velocity of decomposition is high. Thus it is formed when mixtures of water vapour and oxygen are led rapidly over glowing magnesia capillaries, and when a blast of water vapour is blown on to a hydrogen flame. When oxygen is blown on to spark gaps or high voltage arcs ozone is obtained, and when water vapour is substituted for oxygen the product is hydrogen peroxide. In stagnant air the spark gives chiefly nitric oxide. Finally the ozone tube yields hydrogen peroxide if mixtures of oxygen and water at a sufficiently high temperature are led through it. Traces of ozone are also formed.

New Borneol.—Ossian Aschan.—When the hydrochloride of terecamphene (melting-point 148—149°) is treated with bases in presence of water a good yield of a new alcohol $C_{10}H_{17}.OH$ is obtained. Its properties show that it is neither borneol nor isoborneol; for instance, it readily gives up water when it is shaken for a few minutes with dilute mineral acids or boiled for a short time with glacial acetic acid. When it is oxidised it gives only small quantities of camphor and possibly a secondary reaction occurs. The new substance is a tertiary alcohol.

Lecture Experiments to Prepare Iodide Chlorides, Iodo and Iodinium Compounds.—C. Willgerodt.—I. *Preparation of Phenyl Iodide Chloride.*—The inner surface of a cylinder filled with chlorine is wetted with a solution of benzene iodide in chloroform. The chlorine instantly adds itself on to the iodide and crystals of phenyl iodide chloride cover the interior of the cylinder. II. *Preparation of Iodobenzene from Phenyl Iodide Chloride.*—Phenyl iodide chloride is rubbed up with a freshly prepared filtered calcium chloride solution and then boiled. White iodobenzene soon appears, the chlorine escaping quantitatively. The crystals of iodobenzene may be separated by cooling with ice-water. III. *Preparation of Diphenyl Iodinium Chloride and Iodide from Phenyl Iodide Chloride.*—A mixture of phenyl iodide chloride and caustic soda solution is heated till all the solid has disappeared. It is then filtered to separate off drops of benzene iodide, and divided into two parts. To one part concentrated hydrochloric acid is added, and a precipitate of sodium chloride and diphenyl iodinium chloride is at once obtained; the former may be separated by the addition of water. Potassium iodide is added to the second part of the solution, and thus diphenyl iodinium iodide is precipitated in white crystalline masses.

MISCELLANEOUS.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 4th instant, Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Earl Fitzwilliam, Dr. J. O'Conor Donelan, Mr. H. E. Donnithorne, Miss Helen Douglas, Mr. W. L. Dunn, Miss Farrer, Mr. H. E. Harrison, Mr. R. C. B. Kerin, Mrs. Carl Meyer, Lady O'Hagan, and Mr. H. T. Perkins, were elected Members. The Special Thanks of the Members were returned to Mr. J. Y. Buchanan, F.R.S., for his donation of £100 to the Fund for the Promotion of Experimental Research at Low Temperatures. A Resolution of Condolence with the Duchess of Devonshire on the decease of the Duke of Devonshire was passed.

Royal Institution.—On Tuesday next, May 26, at 3 o'clock, Professor W. Stirling begins a course of two lectures at the Royal Institution on "Animal Heat and Allied Phenomena"; and on Saturday, May 30, Dr. H. Walford Davies commences a course of two lectures on "The Art of Bach and Future Developments" (with Musical Illustrations). The Friday Evening Discourse on May 29 will be delivered by Sir Ralph Payne Gallwey, on "Ancient and Mediæval Projectile Weapons other than Firearms"; and on June 5, by Professor Sir James Dewar, on "The Nadir of Temperature and Allied Phenomena."

Chemical Society Research Fund.—A meeting of the Research Fund Committee will be held in June next. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on, or before, Monday, June 8, 1908. All persons who received grants in June, 1907, or in June of any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be in the hands of the Hon. Secretaries not later than Monday, June 1. The Council wish to draw special attention to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is to be more or less especially devoted to the encouragement of research in inorganic and metallurgical chemistry. Furthermore, that the income due to the sum accruing from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the coal-tar and allied industries.

Institute of Metals.—The objects of the Institute are similar to those of the well-known Iron and Steel Institute:—(1) To advance our knowledge of the non-ferrous metals and their alloys, more especially copper, zinc, tin, aluminium, lead, nickel, gold, silver, and platinum. (2) The publication, twice a year, of a volume of abstracts of papers and books on metallurgical subjects, likely to interest members. The volume will be a comprehensive bibliography of the practical and scientific work on non-ferrous metals of each year, both at home and abroad, and will be of great value. (3) To afford a means of communication between members of the trades in question, bearing upon their respective manufactures, excluding all questions connected with wages and trade regulation. (4) To arrange periodical meetings for the purpose of discussing practical and scientific subjects relating to the manufacture, working-up, and use of the non-ferrous metals. It is the desire of the founders to include not merely the copper and brass trades, but the spelter, lead, nickel, aluminium, and silver trades, in fact, all those engaged, producing, or working-up, the non-ferrous metals and their alloys. A Special Meeting is to be held in London on June 10th, at 2.30 p.m., at which the Committee will report progress, and it is hoped formally constitute the proposed Institute. All smelters, manufacturers, merchants, metallurgists, engineers, and scientific men who take an interest in the formation of the Institute of Metals, are requested to send in their names at once to William H. Johnson, care of Rd. Johnson, Clapham, and Morris, Ltd., Manchester, who, during Professor Carpenter's indisposition, has undertaken to act as Secretary.

MEETINGS FOR THE WEEK.

Tuesday, 26th.—Royal Institution, 3. "Animal Heat and Allied Phenomena," by Prof. William Stirling, M.D.
—— Faraday Society, 8. Presidential Address, "Some Aspects of the Work of Lord Kelvin," by Sir Oliver Lodge.

Thursday, 28th.—Royal Institution, 3. "The Chemistry of Photography" by Alexander Scott, F.R.S., &c.

Friday, 29th.—Royal Institution, 9. "Ancient and Mediæval Projectile Weapons other than Firearms," by Sir Ralph Payne-Gallwey, Bart.

Saturday, 30th.—Royal Institution, 3. "The Art of Bach and Future Developments," by H. Walford Davies, Mus. Doc

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THE CHEMICAL NEWS.

Vol. XCVII., No. 2531.

ON THE CALCULATION OF THERMO-CHEMICAL CONSTANTS.

III.—Thermal Constants of Organic Oxygen Compounds.

By H. STANLEY REDGROVE, B.Sc. (Lond.), F.C.S.

We find, generally in compounds of carbon, hydrogen, and oxygen, that the oxygen is combined in three primary ways, namely, the etheric, in which the oxygen atom is singly linked to two different carbon atoms; the hydroxylic, in which the oxygen atom is singly linked to a carbon and to a hydrogen atom; the ketonic, in which the oxygen atom is "doubly" linked to one carbon atom: each of these three classes will require a different constant, as follows hereinafter.

The molecular heats of combustion and formation of aromatic compounds will be calculated by means of the constants ζ = molecular heat of combustion of benzene (at constant volume) = 797·9 cals. (Thomsen), ζ' = molecular heat of formation of benzene (at constant volume) = −13·7 cals. (Thomsen), so that no assumptions regarding the constitution of the benzene nucleus are introduced.

1. *Molecular Heats of Combustion of Ethers.**

All ethers can theoretically be obtained by replacing $2c$ hydrogen atoms in one or more hydrocarbons by c oxygen atoms, each linked to two different carbon atoms, where c is some integer. The following constant will therefore be required:—ω = the algebraic sum of the following heats—(i.) due to the severance of two C.H links; (ii.) due to the combustion of two hydrogen atoms (to liquid water) minus the algebraic sum of the following heats—(iii.) due to the severance of two C.O links; (iv.) one-half that due to the formation of an oxygen molecule; or as it can be more simply written:—

ω = the sum of the following heats—(ii.) due to the combustion of two hydrogen atoms (to liquid water); (iii.) due to the formation of two C.O links, minus the sum of the following heats—(i.) due to the formation of two C.H links; (iv.) one-half that due to the formation of an oxygen molecule.

So that the general ether,—

$$nC+2(n+1-a-2b-p-c)H+(n+p-a-b-1)L_1+aL_2+ +bL_3+cO+2c(C.O)\text{ links},\dagger$$

can be written—

$$nC+2(n+1-a-2b-p)H+ +(n+p\ \ a-b-1)L_1+aL_2+bL_3-c\omega =n\alpha-(n+p\cdot\ a-b-1)\beta-a\gamma-b\delta-c\omega.$$

In Table I. will be found the molecular heats of combustion (corrected for constant volume) of eight ethers, determined by Thomsen; from these the value of ω has been calculated thus:—

Methyl ethyl ether is $CH_3.O.C_2H_5$, *i.e.*, $3\alpha-\beta-\omega$.
M.H.C. found = 504·4 cals.

Therefore $\omega = 3\alpha-\beta-504{\cdot}4$ cals. = (632·4 − 52·5 − 504·4) cals. = 75·5 cals., &c.; these values are given in the table; the mean value of the six more consistent values is ω = 75·4 cals.

Using this value the molecular heats of combustion of all the ethers given have been calculated and are exhibited, together with the differences between them and the experimental, and the percentage errors in Table I., the agreement is quite satisfactory, except, perhaps, in the case of methylal.

The agreement in the case of anisol shows that ω has the same value in aromatic as in aliphatic substances.

2. *Molecular Heats of Formation of Ethers.*

The molecular heat of formation constant corresponding to ω is:—

ω' = the algebraic sum of the following heats—(i.) due to the decomposition of a hydrogen molecule; (ii.) due to the formation of two C.H links, minus the algebraic sum of the following heats—(iii.) one-half that due to the decomposition of an oxygen molecule; (iv.) due to the formation of two C.O links, or as it can be more simply written:—

ω' = the sum of the following heats—(ii.) due to the formation of two C.H links; (iii.) one-half that due to the formation of an oxygen molecule, minus the sum of the following heats—(i.) due to the formation of a hydrogen molecule; (iv.) due to the formation of two C.O links.

Therefore $\omega+\omega'$ = the heat due to the combustion of two hydrogen atoms (to liquid water) less the heat due to the formation of a hydrogen molecule = the molecular heat of combustion of hydrogen gas to liquid water = 67·5 cals.; whence,—

ω' = 67·5 cals. $-\omega$ = (67·5 − 75·4) cals. = −7·9 cals.

In Table I. will be found the molecular heats of formation (at constant volume) of eight ethers given by Thomsen; from these the value of ω' has been calculated in a similar manner as was the value of ω. The mean value is ω' = −7·8 cals., agreeing with the above.

Using this value (ω' = −7·8 cals.) the molecular heats of formation of all the ethers given have been calculated, and are exhibited together with the differences between them and the experimental in Table I.

3. *Molecular Heats of Combustion of Alcohols.*

All alcohols can theoreiically be obtained by replacing d hydrogen atoms in the corresponding hydrocarbon by d hydroxyl groups each linked to carbon, where d is some integer; the following constant will therefore be required:—

ω_1 = the algebraic sum of the following heats—(i.) due to the severance of a C.H link; (ii.) due to the combustion of a hydrogen atom (to liquid water) minus the algebraic sum of the following heats—(iii.) due to the severance of a C.O link; (iv.) due to the severance of an O.H link; (v.) one-half that due to the formation of an oxygen atom; (vi.) due to the combustion of a hydrogen atom (to liquid water); or as it can be more simply written:—

ω_1 = the sum of the following heats—(iii.) due to the formation of a C.O link; (iv.) due to the formation of an O.H. link, minus the sum of the following heats; (i.) due to the formation of a C.H link; (v.) one-half that due to the formation of an oxygen molecule.

So that the general alcohol,—

$$nC+2\left(n+1-a-2b-p-\frac{d}{2}\right)H+(n+p-a-b-1)L_1+ +aL_2+bL_3+d(C.O)\text{ links}+dO+d(O.H)\text{ links}+ +dH\text{ (linked to O, }\textit{not}\text{ to C)},$$

can be written—

$$nC+2(n+1-a-2b-p)H+(n+p-a-b-1)L_1+aL_2+ +bL_3-d\omega_1=n\alpha-(n+p-a-b-1)\beta-a\gamma-b\delta-d\omega_1.$$

Now, the heat of combustion of two hydrogen atoms to water vapour = the heat due to the formation of two O.H links less one-half that due to the formation of an oxygen molecule.

Therefore the heat due to the formation of two O.H links = the heat of combustion of two hydrogen atoms to water vapour plus one-half the heat due to the formation of an oxygen molecule.

Now, $2\omega_1$ = the sum of the following heats—(iii.) due to the formation of two C.O links; (iv.) due to the formation of two O.H links, minus the sum of the following heats—

* The consideration of ethylene oxide is postponed.
† For common ethers put $p=-1$.

TABLE I.—Ethers.

1. Substance.	2. Formula.	Molecular Heats of Combustion. 3. Formula.	4. M.H.C. found (Thomsen) constant vol. Cals.	5. ω Calculated. Cals.	6. M.H.C. calculated. Cals.	7. Difference between cols. 4 and 6. Cals.	8. Error. Per cent.	Molecular Heats of Formation. 9. Formula.	10. M.H.F. (Thomsen) constant vol. Cals.	11. ω′ Calculated. Cals.	12. M.H.F. calculated. Cals.	13. Difference between cols. 10 and 12. Cals.
Dimethyl ether	$CH_3.O.CH_3$	$2\alpha-\omega$	348·2	73·4	346·2	−2·0	−0·57	$2\alpha'-\omega'$	48·2	−5·8	50·2	+2·0
Methylethyl ether	$CH_3.O.C_2H_5$	$3\alpha-\beta-\omega$	504·4	75·5	504·5	+0·1	+0·02	$3\alpha'-\beta'-\omega'$	56·4	−7·8	56·4	0·0
Diethyl ether	$C_2H_5.O.C_2H_5$	$4\alpha-2\beta-\omega$	657·9	(80·3)	662·8	+4·9	+0·74	$4\alpha'-2\beta'-\omega'$	67·4	(−12·6)	62·6	−4·8
Methylallyl ether	$CH_3.O.C_3H_5$	$4\alpha-\beta-\gamma-\omega$	625·7	76·0	626·3	+0·6	+0·10	$4\alpha'-\beta'-\gamma'-\omega'$	32·1	−8·3	31·6	−0·5
Diallyl ether	$C_3H_5.O.C_3H_5$	$6\alpha-2\beta-2\gamma-\omega$	909·4	(72·4)	906·4	−3·0	−0·33	$6\alpha'-2\beta'-2\gamma'-\omega'$	9·9	(−4·7)	13·0	+3·1
Methylpropargyl ether	$CH_3.O.C_3H_3$	$4\alpha-\beta-\delta-\omega$	602·7	75·0	602·3	−0·4	−0·07	$4\alpha'-\beta'-\delta'-\omega'$	−12·4	−7·3	−11·9	+0·5
Anisol	$C_6H_5.O.CH_3$	$\zeta+\alpha-\omega$	934·8	73·9	933·3	−1·5	−0·16	$\zeta'+\alpha'-\omega'$	+13·8	−6·3	+15·3	+1·5
Methylal	$CH_2(OCH_3)_2$	$3\alpha-2\omega$	474·9	78·75	481·6	+6·7	+1·41	$3\alpha'-2\omega'$	85·9	−11·15	79·2	−6·7
		Mean .. .. ω = 75·4							Mean .. .. ω' = −7·8			

TABLE II.—Alcohols.

			ω_1 Calculated.						ω_1' calculated.			
Group 1.												
Phenol	$C_6H_5.OH$	$\zeta-\omega_1$	767·6	30·3	768·2	+0·6	+0·08	$\zeta'-\omega_1'$	16·6	−·30·3	16·0	−0·6
Primary Alcohols—												
Methyl alcohol	$CH_3.OH$	$\alpha-\omega_1$	181·4	29·4	181·1	−0·3	−0·17	$\alpha'-\omega_1'$	50·6	−29·4	50·9	+0·3
Ethyl ,,	$C_2H_5.OH$	$2\alpha-\beta-\omega_1$	339·4	29·7	339·4	0·0	0·00	$2\alpha'-\beta'-\omega_1'$	57·0	−29·6	57·1	+0·1
Propyl ,,	$C_3H_7.OH$	$3\alpha-2\beta-\omega_1$	497·2	30·2	497·7	+0·5	+0·10	$3\alpha'-2\beta'-\omega_1'$	63·7	−30·1	63·3	−0·4
Isobutyl ,,	$(CH_3)_2CH.CH_2.OH$	$4\alpha-3\beta-\omega_1$	656·7	29·0	656·0	−0·7	−0·11	$4\alpha'-3\beta'-\omega_1'$	68·5	−28·7	69·5	+1·0
Isoamyl ,,	$(CH_3)_2CH.CH_2.CH_2.OH$	$5\alpha-4\beta-\omega_1$	818·0	(26·0)	814·3	−3·7	−0·45	$5\alpha'-4\beta'-\omega_1'$	71·7	(25·7)	75·7	+4·0
Allyl ,,	$C_3H_5.OH$	$3\alpha-\beta-\gamma-\omega_1$	463·6	(27·3)	461·2	−2·4	−0·52	$3\alpha'-\beta'-\gamma'-\omega_1'$	29·8	(−27·2)	32·3	+2·5
		Mean .. .. ω_1 = 29·7							Mean .. .. ω_1' = −29·6			
Group 2.												
Propargyl alcohol	$C_3H_3.OH$	$3\alpha-\beta-\delta-\omega_1$	430·2	36·7	430·5	+0·3	+0·07	$3\alpha'-\beta'-\delta'-\omega_1'$	−4·4	−36·5	−4·5	−0·1
Ethylene glycol	$C_2H_4(OH)_2$	$2\alpha-\beta-2\omega_1$	297·2	$71·9\times\frac{1}{2}$	296·3	−0·9	−0·30	$2\alpha'-\beta'-2\omega_1'$	+99·2	$-71·8\times\frac{1}{2}$	+100·2	+1·0
Secondary Alcohol—												
Isopropyl alcohol	$(CH_3)_2CH.OH$	$3\alpha-2\beta-\omega_1$	491·9	35·5	491·0	−0·9	−0·18	$3\alpha'-2\beta'-\omega_1'$	69·0	−35·4	70·0	+1·0
Tertiary Alcohols—												
Trimethylcarbinol	$(CH_3)_3C.OH$	$4\alpha-3\beta\ \omega_1$	639·6	(46·1)	649·3	+9·7	+1·52	$4\alpha'-3\beta'-\omega_1'$	85·7	(−45·9)	76·2	−9·5
Dimethylethylcarbinol	$(CH_3)_2C(OH)C_2H_5$	$5\alpha-4\beta-\omega_1$	808·4	35·6	807·6	−0·8	−0·10	$5\alpha'-4\beta'-\omega_1'$	81·3	−35·3	82·4	+1·1
		Mean .. .. ω_1 = 35·9							Mean .. .. ω_1' = −35·8			
		Final mean (see text) .. .. ω_1 = 36·4										

{Chemical News, May 29, 1908

(i.) due to the formation of two C.H links; (v.) due to the formation of an oxygen molecule.

Hence, substituting the above value for the heat of formation of two O.H links:—

$2\omega_I$ = the sum of the following heats—due to the combustion of two hydrogen atoms to water vapour; (iii.) due to the formation of two C.O links, minus the sum of the following heats—(i.) due to the formation of two C.H links; (v.) one-half that due to the formation of an oxygen molecule (see the definition of ω).

Therefore $2\omega_I$ + the molecular latent heat of steam (corrected for constant volume) = ω.

Therefore $2\omega_I + 9{\cdot}8$ cals. = 75·4 cals., whence ω_I = 32·8 cals.

In Table II. will be found the molecular heats of combustion (corrected for constant volume) of twelve alcohols, &c., determined by Thomsen; from these the values of ω_I have been calculated thus:—

Methyl alcohol is CH_3OH; *i.e.*, $a - \omega_I$. M.H.C. found = 181·4 cals.

Therefore $\omega_I = a - 181{\cdot}4$ cals. = $(210{\cdot}8 - 181{\cdot}4)$ cals. = 29·4 cals., &c.

These values are given in the table. It is seen that the alcohols divide themselves into two groups, thus:—

The first group contains the primary alcohols and phenol, and gives a value for ω_I somewhat below the theoretical (32·8 cals.). The mean of the five more consistent values is ω_I = 29·7 cals. Using this value the molecular heats of combustion of the members of this group have been calculated, and are exhibited, together with the differences between them and the experimental and the percentage errors in Table II. The agreement is quite satisfactory.

The second group contains the secondary and tertiary alcohols, ethylene glycol, and a primary alcohol (propargyl alcohol), and gives a value for ω_I somewhat above the theoretical.

The mean value (neglecting trimethyl carbinol) for this group is 35·9 cals. It will be shown, however, in the next paper in this series that the mean value of ω_I in monocarboxy acids is 37·0 cals. agreeing with this value above; the final mean, namely, 36·4 cals., is used in the calculations, and the molecular heats of combustion of the alcohols in this group have been calculated thereby, and are exhibited, together with the differences between them and the experimental, and the percentage errors in Table II. The agreement is quite satisfactory, except in the case of trimethylcarbinol.

This behaviour of the alcohols in thus dividing themselves into two groups with respect to the value of ω_I is remarkable, inasmuch as it appears that the mere position of the hydroxyl group exercises an influence upon its thermal equivalent, and is in marked contrast to the behaviour of the chlorine substituted hydrocarbons (Chem. News, xcvii., 183).

It may be, however, that the two hydrogen atoms in water are not bound to the oxygen atom with equal affinity; in some alcohols one hydrogen atom is replaced, in others the other hydrogen atom is replaced, depending possibly upon the configuration of the rest of the molecule; whereas the thermal value of either oxygen link with carbon is constant. This would explain why the value of ω_I deduced from a consideration of the ether constant and water is the arithmetic mean between the two values of ω_I obtained from the two groups of alcohols above.

4. *Molecular Heats of Formation of Alcohols.*

The molecular heat of formation constant corresponding to ω_I is:—

ω_I' = the algebraic sum of the following heats—(i.) one-half that due to the decomposition of a hydrogen molecule; (ii.) due to the formation of a C.H link, minus the algebraic sum of the following heats—(iii.) one-half that due to the decomposition of an oxygen molecule; (iv.) one-half that due to the decomposition of a hydrogen molecule; (v.) due to the formation of a C.O link; (vi.) due to the formation of an O.H link, or as it can be more simply written:—

ω_I' = the sum of the following heats—(ii.) due to the formation of a C.H link; (iii.) one-half that due to the formation of an oxygen molecule, minus the sum of the following heats—(v.) due to the formation of a C.O link; (vi.) due to the formation of an O.H link.

Hence, $\omega_I' = -\omega_I$.

In Table II. will be found the molecular heats of formation (at constant volume) of twelve alcohols, &c., given by Thomsen; from these the values of ω_I' have been calculated, similarly as were the values of ω_I. The mean values obtained are:—For the first group, $\omega_I' = -29{\cdot}6$ cals.; for the second group, $\omega_I' = -35{\cdot}8$ cals., in agreement with the above relation.

Using the values obtained from this relation ($\omega_I' = -\omega_I$), namely, $-29{\cdot}7$ cals. and $-36{\cdot}4$ cals., for the first and second groups respectively, the molecular heats of formation of all the alcohols, &c., given have been calculated, and are exhibited together with the differences between them and the experimental in Table II.

The Polytechnic, Regent Street, W.

(To be continued).

THE ETHER OF SPACE.*

By Sir OLIVER LODGE, LL.D., D.Sc., F.R.S.

Thirty years ago Clerk Maxwell gave in this place a remarkable address on "Action at a Distance." It is reported in the *Journal of the Royal Institution*, vol. vii., and to it I would direct attention. Most natural philosophers hold, and have held, that action at a distance across empty space is impossible; in other words, that matter cannot act where it is not, but only where it is. The question "Where is it?" is a further question that may demand attention and require more than a superficial answer. For it can be argued on the hydrodynamic or vortex theory of matter, as well as on the electrical theory, that every atom of matter has a universal though nearly infinitesimal prevalence, and extends everywhere; since there is no definite sharp boundary or limiting periphery to the region disturbed by its existence. The lines of force of an isolated electric charge extend throughout illimitable space. And though a charge of opposite sign will curve and concentrate them, yet it is possible to deal with both charges, by the method of superposition, as if they each existed separately without the other. In that case, therefore, however far they reach, such nuclei clearly exert no "action at a distance" in the technical sense.

Some philosophers have reason to suppose that mind can act directly on mind without intervening mechanism, and sometimes that has been spoken of as genuine action at a distance; but, in the first place, no proper conception or physical model can be made of such a process, nor is it clear that space and distance have any particular meaning in the region of psychology. The links between mind and mind may be something quite other than physical proximity, and in denying action at a distance across empty space I am not denying telepathy or other activities of a non-physical kind; for although brain disturbance is certainly physical and is an essential concomitant of mental action, whether of the sending or receiving variety, yet we know from the case of heat that a material movement can be excited in one place at the expense of corresponding movement in another, without any similar kind of transmission or material connection between the two places: the thing that travels across vacuum is not heat.

In all cases where physical motion is involved, however,

* Abstract of a Discourse delivered at the Royal Institution, February 21, 1908.

I would have a medium sought for; it may not be matter, but it must be something; there must be a connecting link of some kind, or the transference cannot occur. There can be no attraction across really empty space. And even when a material link exists, so that the connexion is obvious, the explanation is not complete; for when the mechanism of attraction is understood, it will be found that a body really only moves because it is pushed by something from behind. The essential force in nature is the *vis a tergo*. So when we have found the "traces," or discovered the connecting thread, we still run up against the word "cohesion," and ought to be exercised in our minds as to its ultimate meaning. Why the whole of a rod should follow, when one end is pulled, is a matter requiring explanation; and the only explanation that can be given involves, in some form or other, a continuous medium connecting the discrete and separated particles or atoms of matter.

When a steel spring is bent or distorted, what is it that is really strained? Not the atoms—the atoms are only displaced; it is the connecting links that are strained—the connecting medium—the ether. Distortion of a spring is really distortion of the ether. All stress exists in the ether. Matter can only be moved. Contact does not exist between the atoms of matter as we know them; it is doubtful if a piece of matter ever touches another piece any more than a comet touches the sun when it appears to rebound from it; but the atoms are connected, as the comet and the sun are connected, by a continuous *plenum* without break or discontinuity of any kind. Matter acts on matter only through the ether. But whether matter is a thing utterly distinct and separate from the ether, or whether it is a specifically modified portion of it—modified in such a way as to be susceptible of locomotion, and yet continuous with all the rest of the ether, which can be said to extend everywhere—far beyond the bounds of the modified and tangible portion—are questions demanding, and I may say in process of receiving, answers.

Every such answer involves some view of the universal and possibly infinite uniform omnipresent connecting medium, the Ether of space.

It has been said, somewhat sarcastically, that the ether was made in England. The statement is only an exaggeration of the truth. I might even urge that it has been largely constructed in the Royal Institution; for, I will remind you now of the chief lines of evidence on which its existence is believed in, and our knowledge of it is based. First of all, Newton recognised the need of a medium for explaining gravitation. In his "Optical Queries" he shows that if the pressure of this medium is less in the neighbourhood of dense bodies than at great distances from them, dense bodies will be driven towards each other; and that if the diminution of pressure is inversely as the distance from the dense body, the law will be that of gravitation.

All that is required, therefore, to explain gravity is a diminution of pressure, or increase of tension, caused by the formation of a matter unit—that is to say, of an electron or corpuscle; and although we do not yet know what an electron is—whether it be a strain centre, or what kind of singularity in the ether it may be—there is no difficulty in supposing that a slight, almost infinitesimal, strain or attempted rarefaction should be produced in the ether whenever an electron came into being—to be relaxed again only on its resolution and destruction. Strictly speaking it is not a real *strain*, but only a "stress"; since there can be no actual *yield*, but only a pull or tension, extending in all directions towards infinity.

The tension required per unit of matter is almost ludicrously small, and yet in the aggregate, near such a body as a planet, it becomes enormous.

The force with which the moon is held in its orbit would be great enough to tear asunder a steel rod four hundred miles thick, with a tenacity of thirty tons per square inch; so that if the moon and earth were connected by steel instead of by gravity, a forest of pillars would be necessary to whirl the system once a month round their common centre of gravity. Such a force necessarily implies enormous tension or pressure in the medium. Maxwell calculates that the gravitational stress near the earth, which we must suppose to exist in the invisible medium, is 3000 times greater than what the strongest steel could stand; and near the sun it should be 2500 times as great as that.

The question has arisen in my mind, whether, if the whole sensible universe—estimated by Lord Kelvin as equivalent to about a thousand million suns—were all concentrated in one body of specifiable density, the stress would not be so great as to produce a tendency towards etherial disruption; which would result in a disintegrating explosion, and a scattering of the particles once more as an enormous nebula and other fragments into the depths of space. On doing the arithmetic, however, I find the necessary concentration absurdly great, showing that such a mass is quite insufficient; see Appendix). For the tension would be a maximum in the interior of such a mass; and, if it rose to the value 10^{38} dynes per square centimetre, something would have to happen. I do not suppose that this can be the reason, but one would think there must be *some* reason, for the scattered condition of gravitative matter.

Too little is known, however, about the mechanism of gravitation to enable us to adduce it as the strongest argument in support of the existence of an ether. The oldest valid and conclusive requisition of an etherial medium depends on the wave theory of light, one of the founders of which was your Professor of Natural Philosophy at the beginning of last century, Dr. Thomas Young.

No ordinary matter is capable of transmitting the undulations or tremors that we call light. The speed at which they go, the kind of undulation, and the facility with which they go through vacuum, forbid this.

So clearly and universally has it been perceived that waves must be waves of something—something distinct from ordinary matter—that Lord Salisbury, in his presidential address to the British Association at Oxford, criticised the ether as little more than a nominative case to the verb to undulate. It is truly *that*, though it is also truly more than that; but to illustrate that luminiferous aspect of it, I will quote a paragraph from that lecture of Clerk Maxwell's to which I have already referred:—

"The vast interplanetary and interstellar regions will no longer be regarded as waste places in the universe, which the Creator has not seen fit to fill with the symbols of the manifold order of His kingdom. We shall find them to be already full of this wonderful medium; so full, that no human power can remove it from the smallest portion of space, or produce the slightest flaw in its infinite continuity. It extends unbroken from star to star; and when a molecule of hydrogen vibrates in the dog-star the medium receives the impulses of these vibrations, and after carrying them in its immense bosom for several years, delivers them, in due course, regular order, and full tale, into the spectroscope of Mr. Huggins, at Tulse Hill." (It is pleasant to remember that those veteran investigators, Sir William and Lady Huggins, are still at work).

This will suffice to emphasise the fact that the eye is truly an etherial sense-organ—the only one which we possess, the only mode by which the ether is enabled to appeal to us, and that the detection of tremors in this medium—the perception of the direction in which they go, and some inference as to the quality of the object which has emitted them—cover all that we mean by "sight" and "seeing."

I pass then to another function, the electric and magnetic phenomena displayed by the ether; and on this I will only permit myself a very short quotation from the writings of Faraday, whose whole life may be said to have been directed towards a better understanding of these ethereous phenomena. Indeed the statue in your entrance hall may be considered as the statue of the discoverer of the electric and magnetic properties of the Ether of space.

Faraday conjectured that the same medium which is concerned in the propagation of light might also be the agent in electromagnetic phenomena. "For my own part," he says, "considering the relation of a vacuum to the magnetic force, and the general character of magnetic phenomena external to the magnet, I am much more inclined to the notion that in the transmission of the force there is such an action, external to the magnet, than that the effects are merely attraction and repulsion at a distance. Such an action may be a function of the æther; for it is not unlikely that, if there be an æther, it should have other uses than simply the conveyance of radiation."

This conjecture has been amply strengthened by subsequent investigations.

One more function is now being discovered; the ether is being found to constitute matter—an immensely interesting topic, on which there are many active workers at the present time. I will make a brief quotation from your present Professor of Natural Philosophy (J. J. Thomson), where he summarises the conclusion which we all see looming before us, though it has not yet been completely attained, and would not by all be similarly expressed:—

"The *whole* mass of any body is just the mass of ether surrounding the body which is carried along by the Faraday tubes associated with the atoms of the body. In fact, all mass is mass of the ether; all momentum, momentum of the ether; and all kinetic energy, kinetic energy of the ether. This view, it should be said, requires the density of the ether to be immensely greater than that of any known substance."

Yes, far denser—so dense that matter by comparison is like gossamer, or a filmy imperceptible mist, or a milky way. Nor unreal or unimportant—a cobweb is not unreal, nor to certain creatures is it unimportant, but it cannot be said to be massive or dense; and matter, even platinum, is not dense when compared with the ether. Not till last year, however, did I realise what the density of the ether must really be (see Lodge, *Phil. Mag.*, April, 1907), compared with that modification of it which appeals to our senses as matter, and which for that reason engrosses our attention. If I have time I will return to that before I have finished.

Is there any other function possessed by the ether which, though not yet discovered, may lie within the bounds of possibility for future discovery? I believe there is, but it is too speculative to refer to, beyond saying that it has been urged as probable by the authors of "The Unseen Universe," and has been thus tentatively referred to by Clerk Maxwell:—

"Whether this vast homogeneous expanse of isotropic matter is fitted not only to be a medium of physical interaction between distant bodies, and to fulfil other physical functions of which, perhaps, we have as yet no conception, but also . . . to constitute the material organism of beings exercising functions of life and mind as high or higher than ours are at present—is a question far transcending the limits of physical speculation."

And there for the present I leave that aspect of the subject.

I shall now attempt to illustrate some relations between ether and matter.

The question is often asked, is ether material? This is largely a question of words and convenience. Undoubtedly, the ether belongs to the material or physical universe, but it is not ordinary matter. I should prefer to say it is not "matter" at all. It may be the substance or substratum or material of which matter is composed, but it would be confusing and inconvenient not to be able to discriminate between matter on the one hand and ether on the other. If you tie a knot on a bit of string, the knot is composed of string, but the string is not composed of knots. If you have a smoke or vortex-ring in the air, the vortex-ring is made of air, but the atmosphere is not a vortex-ring; and it would be only confusing to say that it was.

The essential distinction between matter and ether is that matter *moves*, in the sense that it has the property of locomotion and can effect impact and bombardment; while ether is *strained*, and has the property of exerting stress and recoil. All potential energy exists in the ether. It may vibrate, and it may rotate, but as regards locomotion it is stationary—the most stationary body we know—absolutely stationary, so to speak; our standard of rest.

All that we ourselves can effect, in the material universe, is to alter the motion and configuration of masses of matter; we can move matter, by our muscles, and that is all we can do directly: everything else is indirect.

But now comes the question, how is it possible for matter to be composed of ether? How is it possible for a solid to be made out of fluid? A solid possesses the properties of rigidity, impenetrability, elasticity, and such like; how can these be imitated by a perfect fluid such as the ether must be? The answer is, they can be imitated by a fluid in motion; a statement which we make with confidence as the result of a great part of Lord Kelvin's work.

It may be illustrated by a few experiments.

A wheel of spokes, transparent or permeable when stationary, becomes opaque when revolving, so that a ball thrown against it does not go through, but rebounds. The motion only affects permeability to matter; transparency to light is unaffected.

A silk cord hanging from a pully becomes rigid and viscous when put into rapid motion; and pulses or waves which may be generated on the cord travel along it with a speed equal to its own velocity, whatever that velocity may be, so that they appear to stand still. This is a case of kinetic rigidity; and the fact that the wave-transmission velocity is equal to the rotatory speed of the material is typical and important, for in all cases of kinetic elasticity these two velocities are of the same order of magnitude.

A flexible chain, set spinning, can stand up on end while the motion continues.

A jet of water at sufficient speed can be struck with a hammer, and resists being cut with a sword.

A spinning disk of paper becomes elastic like flexible metal, and can act like a circular saw. Sir William White tells me that in naval construction steel plates are cut by a rapidly revolving disk of soft iron.

A vortex-ring, ejected from an elliptical orifice, oscillates about the stable circular form, as an indiarubber ring would do; thus furnishing a beautiful example of kinetic elasticity, and showing us clearly a fluid displaying some of the properties of a solid.

A still further example is Lord Kelvin's model of a spring balance, made of nothing but rigid bodies in spinning motion. (Address to Section A of British Association at Montreal, 1884).

If the ether can be set spinning, therefore, we may have some hope of making it imitate the properties of matter, or even of constructing matter by its aid. But how are we to spin the ether? Matter alone seems to have no grip of it. I have spun steel disks, a yard in diameter, 4000 times a minute, have sent light round and round between them, and tested carefully for the slightest effect on the ether. Not the slightest effect was perceptible. We cannot spin ether mechanically.

But we can vibrate it electrically; and every source of radiation does that. An electrified body, in sufficiently rapid vibration, is the only source of ether-waves that we know; and if an electric charge is suddenly stopped, it generates the pulses known as X-rays, as the result of the collision. Not speed, but sudden change of speed, is the necessary condition for generating waves in the ether by electricity.

We can also infer some kind of rotary motion in the ether; though we have no such obvious means of detecting the spin as is furnished by vision for detecting some kinds of vibration. It is supposed to exist whenever we put a charge into the neighbourhood of a magnetic pole. Round the line joining the two the ether is spinning like a top. I

do not say it is spinning fast: that is a question of its density; it is in fact spinning with excessive slowness, but it is spinning with a definite moment of momentum. J. J. Thomson's theory makes its moment of momentum exactly equal to $e\,m$, the product of charge and pole; the charge being measured electrostatically and the pole magnetically.

How can this be shown experimentally? Suppose we had a spinning top enclosed in a case, so that the spin was unrecognisable by ordinary means—it could be detected by its gyrostatic behaviour to force. If allowed to "precess" it will respond by moving perpendicularly to a deflecting force. So it is with the charge and the magnetic pole. Try to move the charge suddenly, and it immediately sets off at right angles. A moving charge is a current, and the pole and the current try to revolve round one another—a true gyrostatic action due to the otherwise unrecognisable etherial spin. The fact of such magnetic rotation was discovered by Faraday.

I know that it is usually worked out in another way, in terms of lines of force and the rest of the circuit; but I am thinking of a current as a stream of projected charges; and no one way of regarding such a matter is likely to exhaust the truth, or to exclude other modes which are equally valid. Anyhow, in whatever way it is regarded, it is an example of the three rectangular vectors.

The three vectors at right angles to each other, which may be labelled Current, Magnetism, and Motion respectively, or more generally E, H, and V, represent the quite fundamental relation between ether and matter, and constitute the link between Electricity, Magnetism, and Mechanics. Where any two of these are present, the third is a necessary consequence. This principle is the basis of all dynamos, of electric motors, of light, of telegraphy, and of most other things. Indeed, it is a question whether it does not underlie everything that we know in the whole of the physical sciences; and whether it is not the basis of our conception of the three dimensions of space.

Lastly, we have the fundamental property of matter called *inertia*, which, if I had time, I would show could be explained electro-magnetically, provided the etherial density is granted as of the order 10^{12} grms. per cubic centimetre. The elasticity of the ether would then have to be of the order 10^{33} c.g.s.; and if this is due to intrinsic turbulence, the speed of the whirling or rotational elasticity must be of the same order as the velocity of light. This follows hydrodynamically; in the same sort of way as the speed at which a pulse travels on a flexible running endless cord, whose tension is entirely due to the centrifugal force of the motion, is precisely equal to the velocity of the cord itself. And so, on our present view, the intrinsic energy of constitution of the ether is incredibly and portentously great; every cubic millimetre of space possessing what, if it were matter, would be a mass of a thousand tons, and an energy equivalent to the out-put of a million-horse-power-station for forty million years.

The universe we are living in is an extraordinary one; and our investigation of it has only just begun. We know that matter has a psychical significance, since it can constitute *brain*, which links together the physical and the psychical worlds. If anyone thinks that the ether, with all its massiveness and energy, has probably no psychical significance, I find myself unable to agree with him.

(To be continued).

New Method of Determining Phosphorus in Organic Matter.—Isidor Bay.—The organic matter is ignited in a tube with sodium carbonate and magnesia. The contents of the tube are dissolved in dilute acetic acid, and the phosphorus is determined in the solution by means of a titrated uranium nitrate solution, using potassium ferrocyanide as an indicator.—*Comptes Rendus*, cxlvi., No. 15.

PROCEEDINGS OF SOCIETIES.

THE ROYAL SOCIETY.

Conversazione, *May 13th*, 1908.

Sir William Crookes exhibited—

1. Scandium, its Salts, and its position in the Scheme of the Chemical Elements.

Scandium is an exceedingly rare terrestrial element, occurring in very few minerals and in very small amount—usually not more than 0·01 per cent. The one exception is the rare mineral wiikite which contains scandium in considerable quantity.

Astronomical research has demonstrated the presence of scandium in comparative abundance in the sun and some of the brighter stars. To enable its spectrum lines to be identified with certainty, especially in some of the fainter celestial bodies, a thorough examination of its spectrum has been undertaken.

2. Rare Minerals containing Scandium: Auerlite, keilhauite, orthite, urdite, wiikite.

3. Salts of Scandium.

Scandium oxide, Sc_2O_3.
Scandium hydroxide, $Sc_2O_3,3H_2O = Sc(OH)_3$.
Scandium carbonate, $Sc_2(CO_3)_3,12H_2O$.
Hydrated scandium chlorides,—

$$Sc_2Cl_6,12H_2O = Sc_2O_3,6HCl,9H_2O,$$
$$Sc_2Cl_6,3H_2O = Sc_2O_3 + 6HCl.$$

Hydrated scandium bromides, $Sc_2Br_6,12H_2O$,

$$Sc_2Br_6,3H_2O = Sc_2O_3,6HBr.$$

Scandium chlorate.
Scandium perchlorate.
Scandium bromate.
Scandium sulphates,—

$$Sc_2(SO_4)_3,6H_2O, \qquad Sc_2(SO_4)_3,5H_2O.$$

Anhydrous scandium sulphate, $Sc_2(SO_4)_3$.
Basic scandium sulphate, $Sc_2O(SO_4)_2$.
Scandium and potassium double sulphate,—

$$3K_2SO_4,Sc_2(SO_4)_3.$$

Scandium selenates,—

$$Sc_2(SeO_4)_3,8H_2O, \qquad Sc_2(SeO_4)_3,2H_2O.$$

Scandium nitrates, $Sc(NO_3)_3,4H_2O$, $Sc(NO_3)_3$, $ScOH(NO_3)_2H_2O$, $Sc_2O(NO_3)_4$.
Scandium formate, $(HCOO)_2ScOH,H_2O$.
Scandium acetate, $(CH_3COO)_2ScOH,2H_2O$.
Scandium propionate, $C_2H_5COO)_2ScOH$.
Scandium butyrate, $(CH_3.CH_2.CH_2.COO)_2ScHO$.
Scandium iso-butyrate,—

$$\left(\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH.COO\right)_2ScOH,2H_2O,$$

Scandium iso-valerate, $(C_4H_9COO)_2ScOH,2H_2O$.
Scandium oxalates,—

$$Sc_2(C_2O_4)_3,5H_2O, \qquad Sc_2(C_2O_4)_3,3H_2O,$$
$$Sc_2(C_2O_4)_3,2H_2O_3, \qquad Sc_2(C_2O_4),H_2O.$$

Scandium picrates, $[C_6H_2(NO_2)_3O]_2ScOH),14H_2O$,
$[C_6H_2(NO_2)_3O]_2,ScOH,5H_2O$.
Scandium pyromellitate.
Scandium camphorate, $C_8H_{14}<\begin{matrix}COO\\COO\end{matrix}>ScOH$.

4. Photographed Spectra of Scandium and associated elements, from λ6305 to λ2625.

5. Lemniscate Curve, showing the author's scheme of the arrangement of the chemical elements in space, and the position of scandium with reference to its associated elements.

Such a figure will result from three very simple simultaneous motions. First, an oscillation to and fro (suppose east and west); secondly, an oscillation at right

angles to the former (suppose north and south); and thirdly, a motion at right angles to these two (suppose downwards), which, in its simplest form, would be with unvarying velocity.

Take any arbitrary and convenient figure-of-eight, without reference to its exact nature, divide each of the loops into eight equal parts, and then drop from these points ordinates corresponding to the atomic weights of the first cycle of elements. The model represents this figure projected in space; in it the elements are supposed to follow one another at equal distances along the figure-of-eight spiral, a gap of one division being left at the point of crossing. The vertical height is divided into 240 equal parts on which the atomic weights are plotted, from H = 1 to Ur = 239·59. The elements falling one under the other along each of the vertical ordinates, are :—

H	He	Li	Gl	B	C	N	O		F			Na	Mg	Al	Si	P	S
Cl	Ne	K	Ca	Sc	Ti	V	Cr	(Mn.	Fe.	Ni.	Co)	Cu	Zn	Ga	Ge	As	Se
Br	Ar	Rb	Sr	Y	Zr	Cb	Mo	(Rh.	Ru.	Pd)		Ag	Cd	In	Sn	Sb	Te
I	Kr	Cs	Ba	Yb	Th	Ta	W	(La.	Ce.	Pr.	Nd)	Au	Hg	Tl	Pb	Bi	
			Ra				Ur	(Ir.	Pt.	Os)							

The four elements, boron, scandium (Mendeleeff's "*ekaboron*, next on order to boron"), yttrium and ytterbium, have a close relationship, thus :—

B	atomic weight	11·0	× 16	= 176·0
Sc	,,	44·1	× 4	= 176·4
Y	,,	89·0	× 2	= 178·0
Yb	,,	173·0	× 1	= 173·0

CHEMICAL SOCIETY.

Ordinary Meeting, May 7th, 1908.

Prof. E. Divers, F.R.S., in the Chair.

Mr. K. S. Caldwell was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Charles Duncan Cooper, 776, Oxford Road, Reading; John Robert Cowburn, Belmont Villa, Birkbeck Grove, Acton, W.; Kaufman George Falk, B.Sc., Ph.D., 1070, Madison Avenue, New York City; Norman Holland, 4907, Sherbrooke Street W., Montreal; James Kirkman King, B.A., 55, Brewery Road, Plumstead; Lionel Gordon Larmuth, Grove House, Cheadle Hulme, Manchester; Henry Robert Lyell, Redcott, Dacres Road, Sydenham, S.E.; Haradham Ray, M.A., 4, Jhamapooker Lane, Calcutta; William Readwin, 6, Kirkfield Terrace, Morley, near Leeds; Alexander Mackintosh Stewart, Penang, Straits Settlements; Herbert Horace Ward, University College of Wales, Aberystwyth; Charles Harold Wright, B.A., Government Laboratory, Port of Spain, Trinidad; Charles Robert Young, B.Sc., 11, Low Pavement, Nottingham.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected :—Arthur John Allmand, M.Sc.; William Henry Benson Baker, B.A.; Josiah Leonard Bowen; Arthur Edward Coverdale; Bidhu Bhushan Dutt, M.A.; Albert Edward Findley, B.Sc.; Atul Chandra Gañguli, B.A.; Charles Gilling; Leonard Clifford Green, B.E.; William Hall, B.Sc.; Cyril Arden Hinds; George Edward Holden; Percy Hulme Hornby; Arthur Horrobin; Hugo Stefan Kohn, Ph.D.; Gerald Roche Lynch; Herbert Mansfield, B.Sc.; Frederick J. Maywald; Alwyne Harcourt Meade; Samuel Ernest Melling; Herbert Richard Neech; Pañchanan Neogi, M.A.; Thomas Richards Phillips; Francis Edward Richards, B.Sc.; William Seelhorst; Edwin John Watkins; William Wheatley, B.A.

Of the following papers, those marked * were read :—

*89. "*The Refraction and Dispersion of Triazo-compounds.*" By James Charles Philip.

The molecular refraction and dispersion of a number of compounds containing the triazo-group have been determined. A study of these constants shows that the contribution which the N_3-group normally makes to the molecular refraction is 8·91 units, almost the same value as the atomic refraction of bromine. The contribution which the N_3-group normally makes to the molecular dispersion is 0·36—0·37, whilst the atomic dispersion of bromine is 0·35. In certain compounds, namely, ethyl triazoformate, phenylazoimide, and α-naphthylazoimide, the refractive and dispersive powers of the N_3-group are considerably above the normal values. Such "optical exaltation" (Brühl, *Ber.*, 1907, xl., 878) is generally associated with the existence in the molecule of contiguous unsaturated groups, and it will be seen that in each of the three triazo-compounds mentioned the N_3-group is in conjugation with an unsaturated group. The bearing of these results on the formulation of the N_3-group was discussed.

*90. "*The Dissociation Constants of Triazoacetic and α-Triazopropionic Acids.*" By James Charles Philip.

The conductivity of solutions of these acids has been determined in the usual way. The values obtained for the expression $k = \alpha^2(1-\alpha)v$ diminish to some extent as the dilution increases, but are sufficiently constant to indicate the strengths of the two acids. The value of k for triazoacetic acid is 0·00090—0·00100, whilst that for α-triazopropionic acid is slightly less, about 0·00086. These values show that the introduction of the N_3-group into the molecule of acetic or propionic acid increases the strength of the acid nearly as much as the introduction of a bromine atom. It is noteworthy, also, that the conductivity of the triazoacetate ion is the same as that of the monobromoacetate ion.

Discussion.

Mr. H. Stanley Redgrove called attention to a paper (Chemical News, 1907, xcv., 193) in which he proved that in general the alleged atomic constants employed in calculating additive physico-chemical constants (such as Brühl's mol.-refractivity constants) were incorrect, and, in the present state of our knowledge, unobtainable.

This was due to the fact that the specific influence due to certain linkings (for example, the "ethane" carbon linking) is neglected. In the paper quoted, he had outlined a general method of calculation by means of the so-called "fundamental constants," whereby the above assumption is avoided, and was applying it with success to the calculation of thermal constants.

Allowing for this, Brühl's hydrogen constant was really the value of the hydrogen atom plus the C.H link decreased by half the value of a C·C link, and his carbon constant the value of the carbon atom increased by twice the value of a C·C link, &c., so that the triazo-constant would be the value of the triazo-group plus the link joining it to carbon decreased by half the value of a C·C link.

*91. "*The Fermentation of Mannose and Lævulose by Yeast-juice.*" (Preliminary Note). By Arthur Harden and William John Young.

1. Mannose is fermented by yeast-juice at almost the same rate as dextrose.

2. Lævulose is fermented somewhat more rapidly than dextrose, the rate varying with different samples of yeast-juice from 1·2 to 1·8, compared with that of dextrose = 1.

3. Mannose and lævulose behave qualitatively towards phosphates in the presence of yeast-juice in a similar manner to dextrose.

a. When a phosphate is added to a fermenting mixture containing either of these sugars, the phosphate is converted into a hexosephosphate not precipitable by magnesia mixture; the rate of fermentation is temporarily greatly accelerated, and during this period an extra amount of carbon dioxide is evolved, equivalent to the phosphate added; the rate then rapidly diminishes, and falls to a value equal to, or slightly greater than, that which it had before the addition of the phosphate.

The fermentation of mannose and lævulose by yeast-juice therefore probably proceeds according to the same

two equations as have been previously proposed by the authors for dextrose :—

1. $2C_6H_{12}O_6 + 2R_2'HPO_4 = 2CO_2 + 2C_2H_6O + C_6H_{10}O_4(PO_4R_2')_2 + 2H_2O$.
2. $C_6H_{10}O_4(PO_4R_2')_2 + 2H_2O = C_6H_{12}O_6 + 2R_2'HPO_4$.

b. As in the case of dextrose, an optimum concentration of phosphate exists, which produces a maximum rate of fermentation. Increase of concentration beyond this maximum diminishes the rate of fermentation produced, until, with a sufficiently great concentration of phosphate, the rate is less than that of the juice in the absence of added phosphate.

4. The quantitative relations of mannose to phosphates are practically the same as those of dextrose.

The maximum rate produced by lævulose, on the other hand, is much greater than (about double) that produced by dextrose or mannose. The accelerated fermentation of lævulose in presence of phosphate, moreover, is much less readily inhibited than that of dextrose or mannose by the further addition of phosphate, the difference in this respect being very marked.

5. Lævulose possesses the property of inducing rapid fermentation in a mixture of dextrose or mannose with yeast-juice, in which fermentation has been inhibited by a large excess of phosphate and in which the concentration of free phosphate is maintained constant throughout the experiment. Dextrose and mannose have not a similar power. The amount of lævulose required to produce this effect is comparatively small. Thus, for a mixture of 15 cc. of yeast-juice with 15 cc. of a 0·6 molar solution of potassium phosphate and 2 grms. of dextrose fermenting at the rate of 0·7 cc. per five minutes, the addition of 0·05 grm. of lævulose was found to be sufficient, the maximum rate produced being 17 cc. per five minutes. The effect is not due to the preferential fermentation of the lævulose, as the amount of gas evolved far exceeds that which could be derived from this source.

The nature of this reaction is still under investigation.

Discussion.

Mr. Grant Hooper asked if Dr. Harden had examined the effect of phosphates on yeast as distinct from yeast-juice. In view of the fact that phosphates had been often used in the so-called "yeast foods" offered to or employed by brewers, it would be interesting to know whether the authors had observed whether the addition of phosphate to normal fermentations with yeast had the same effect as when added to yeast-juice.

Dr. Harden, in his reply, said that Slator had recently observed that the fermentation caused by yeast was not accelerated by phosphate.

*92. "*The Constituents of Olive Leaves*." By Frederick Belding Power and Frank Tutin.

Air-dried olive leaves were percolated with hot alcohol, when they gave about 30 per cent of their weight of extracted material. This alcoholic extract yielded, besides some amorphous matter, the following products :—

(1) A new *monocarboxylic acid*, $C_{22}H_{45}\cdot CO_2H$ (m. p. 68—69°) ; (2) a small amount of a mixture of fatty acids, containing oleic acid ; (3) hentriacontane, $C_{31}H_{64}$ (m. p. 68—69°) ; (4) pentatriacontane, $C_{35}H_{72}$ (m. p. 74·5°) ; (5) *oleasterol*, $C_{20}H_{34}O$ (m. p. 174°), a new, crystalline alcohol related to the phytosterols ; (6) a new, crystalline alcohol, *olestranol*, $C_{25}H_{42}O_2$ (m. p. 217—218°), which appears to be a hydroxyphytosterol ; (7) *homo-olestranol*, $C_{27}H_{46}O_2$ (m. p. 210°) ; $[\alpha]_D$ +71°), a compound similar to olestranol ; (8) an amount of *d*-mannitol equivalent to about 3·4 per cent of the weight of air-dried leaves ; (9) a considerable amount of a sugar which yields *d*-phenylglucosazone ; (10) a trace of an essential oil ; (11) *oleanol*, $C_{31}H_{48}O(OH)_2,H_2O$ (m. p. 303—304° ; $[\alpha]_D$ +78·3°), a new, crystalline substance in an amount equivalent to nearly 3·4 per cent of the weight of air-dried leaves. This compound contains one alcoholic and one phenolic hydroxyl group. *Monomethyloleanol*, $C_{31}H_{48}O(OH)\cdot O\cdot CH_3$, melts at 194—195°, and on acetylation yields *acetylmethyloleanol*, $C_{31}H_{48}O_2(O\cdot CH)_3\cdot CO\cdot CH_2$ (m.p. 215·5°). *Diacetyloleanol*, $C_{31}H_{48}O_3(CO\cdot CH_3)_2$, when heated to about 210°, gives a *substance*, $C_{31}H_{48}O_3$, which does not fuse at 310°. *Monoacetyloleanol*, $C_{31}H_{48}O_2(OH)\cdot CO\cdot CH_3$, melts at 258°.

*93. "*The Constituents of Olive Bark*." By Frederick Belding Power and Frank Tutin.

Air-dried olive bark, on percolation with hot alcohol, yielded about 30 per cent of its weighed of extracted material. From this alcoholic extract the following crystalline compounds were obtained, together with some amorphous products.

(1) A new *monocarboxylic acid*, $C_{34}H_{67}\cdot CO_2H$ (m. p. 69—70°), which yields an *ethyl* ester melting at 63° ; (2) a new *monocarboxylic acid*, $C_{24}H_{45}\cdot CO_2H$ (m. p. 79°), the *ethyl* ester of which melts at 66·5° ; (3) a new *monocarboxylic acid*, $C_{34}H_{69}\cdot CO_2H$ (m. p. 92°), which yields an *ethyl* ester melting at 87° ; (4) a new *monocarboxylic acid*, $C_{29}H_{57}\cdot CO_2H$ (m. p. 84°), the *ethyl* ester of which melts at 75° ; (5) a *substance*, probably a *tertiary alcohol*, $C_{35}H_{68}O$ (m. p. 70°) ; (6) pentatriacontane, $C_{35}H_{72}$ (m. p. 74—75°) ; (7) a phytosterol, $C_{27}H_{46}O$ (m. p. 136° ; $[\alpha]_D$ −35·2°), which yields an acetyl derivative melting at 119·5° ; (8) a *substance*, $C_{23}H_{38}O_2(OH)_2$ (m. p. 285—290°), which yields an *acetyl* derivative melting at 160°, and is identical with *ipuranol*, a compound recently isolated by Power and Rogerson from *Ipomoea purpurea* ; (9) a new phenolic substance, *olenitol*, $C_{14}H_{10}O_6$ (m. p. 265°), dilute solutions of which show a blue fluorescence. *Acetylolenitol* melts at 130° ; (10) *d*-mannitol, in an amount equivalent to 1·9 per cent of the weight of air-dried bark ; (11) a sugar which yields *d*-phenylglucosazone.

94. "*The Reaction of Diazonium Salts with Mono- and Di-hydric Phenols and with Naphthols*." By Kennedy Joseph Previté Orton and Reginald William Everatt.

The behaviour of a series of typical diazonium salts, mainly hydrogen sulphates, with phenols in alcohol, water, and other solvents has been examined. All diazonium salts couple quantitatively with α- and β-naphthols in alcoholic media, but under similar conditions these salts do not combine with monohydric phenols.

The dihydric phenols, resorcinol and orcinol, resemble the naphthols, reacting readily with all diazonium salts in alcoholic solution. In aqueous solution, on the other hand, only those diazonium salts with a preponderance of negative substituents (halogen atoms) in the benzene nucleus couple completely with the two dihydric phenols. In other cases, unless the acidity has been reduced by sodium acetate, the coupling is either partial or absent, according to the character of the substituents of the benzene nucleus.

It is a remarkable fact that those diazonium salts possessing halogen atoms in the positions 2, 4, and 6 with respect to the diazo-group (for example, *s*-tribromodiazobenzene) will react rapidly and quantitatively with resorcinol and orcinol in solution in 50 per cent sulphuric acid.

Diazonium salts are converted by quinol in aqueous or alcoholic solution into the corresponding hydrocarbon, thus :—

$$Ar\cdot N_2HSO_4 + OH\cdot C_6H_4\cdot OH = ArH + N_2 + H_2SO_4 + O : C_6H_4 : O.$$

With catechol, either coupling or a similar reaction to that with quinol takes place, according to the nature of the substituents in the benzene nucleus of the diazonium salt.

A number of azoresorcinols and azo-orcinols were described.

95. "*The Condensation of Benzoin with Methyl Alcohol*." By James Colquhoun Irvine and David McNicoll.

It has already been noticed (*Trans*., 1907, xci., 1384) that during the methylation of benzoin by Fischer's method two by-products (m. p. 185° and 285°) are formed in varying quantity, according to the conditions of the reaction. As one of the compounds appeared to be produced by the

condensation of benzoin methyl ether, the constitution and mode of formation of both substances have been further examined. The results show that the compounds are tetraphenylfuran derivatives, and the formulæ previously suggested are therefore no longer tenable. Both substances give the same triacetyl derivative when treated with acetic anhydride and sulphuric acid in the cold, and this in turn, when warmed with the reagent, is converted into acicular dibenzoylstilbene. The compound of lower melting-point is converted into the other by the action of methyl alcohol and hydrogen chloride, and both substances are formed when dibenzoylstilbene is subjected to a similar reaction. The compound melting at 185° is thus regarded as *αβ-dibenzoyl-α-methoxydibenzyl*—

$$C_6H_5\cdot C(OMe)\cdot C_6H_5$$
$$C_6H_5\cdot C<\begin{matrix}O\\O\end{matrix}>C\cdot C_6H_5 \quad ,$$

and the second compound (m. p. 285°) as *2-hydroxy* 3 : 5-*dimethoxytetraphenyltetrahydrofuran*, conclusions which are supported by the action of hydrogen iodide on each. Apparently the formation of the compounds takes place during the methylation prior to the formation of benzoin methyl ether, and is doubtless owing to the dehydration of the benzoin to form dibenzoylstilbene, which then unites with two molecules of methyl alcohol in two successive stages.

The occurrence of similar side reactions has also been noticed in the methylation of anisoin.

96. "*The Mutual Solubility of 2-Methylpiperidine and Water.*" By Otto Flaschner and Basil MacEwen.

The influence of constitution on one of the two critical solution temperatures of mutually soluble liquids was discussed. Nitrogen and oxygen atoms increase the mutual solubility when one of the liquids is water, whilst carbon and hydrogen atoms decrease it. In order to ascertain the influence of the position of a substituted group in a cyclic compound, the mutual solubility of 2-methylpiperidine and water has been examined. This is represented by a closed curve. The lower critical solution temperature is 79°, and the higher one 227°.

97. "*The Melting-points of the Anilides, p-Toluidides, and α-Naphthalides of the Normal Fatty Acids.*" By Philip Wilfred Robertson.

The melting-points of the fatty amides do not exhibit any regularity even if the odd or even members are considered separately. The anilides also show the same exceptional behaviour, and, in order to obtain a more definite insight into the relationship between melting-point and number of carbon atoms in a homologous series, the missing members have been prepared as well as a complete series of the *p*-toluidides. The irregularities in these two series seem to tend always in the reverse direction to those observed in the case of the amides. On taking the mean melting-points of the amides and anilides, and of the amides and *p*-toluidides, the disturbing factor, which is considered to be a function of the lack of symmetry of the molecule, is to a great extent eliminated, as regular series of numbers are obtained.

In the fatty *α*-naphthalides, where the substituent group is heavier, irregularities tend to disappear: the melting-points of the even members descend to a minimum at the eighth member and then rise gradually, whilst there is a corresponding minimum in the case of the odd series at the ninth member.

98. "*The Absorption Spectrum of Camphor.*" By Walter Noel Hartley.

The absorption spectrum of solutions of camphor was examined in 1881 (Hartley, *Trans.*, xxxix., 153) and compared with the spectra of benzene and its derivatives. There was a difficulty in obtaining it free from impurities showing absorption bands. Camphor sublimed in sunlight and condensed in large crystals, showed no band, and was remarkably diactinic. In view of more recent work, it was decided to re-examine the spectrum of camphor very carefully. The result has been to show that when solutions of ten times the concentration usually employed in such experiments are examined, a band occurs in the spectrum, due to the occurrence of the CO and CH_2 groups in the molecule. This is in general agreement with the work of Baly, Marsden, and Stewart (*Trans.*, 1906, lxxxix, 979), but otherwise the substance is remarkably diactinic.

99. "*The Viscosity of Solutions.*" By Charles Edward Fawsitt.

In continuation of previous work (*Zeit. Phys. Chem.*, 1904, xlviii., 585; *Electrochemist and Metallurgist*, 1904, iii., 664), a number of colloidal solutions and alcoholic solutions have been examined. In dilute solutions, the viscosity is, in general, a linear function of the concentration. If the viscosities of solutions of the substances in a homologous series are compared, the relation of viscosity to composition appears to be largely additive.

100. "*The Action of Fused Potassium Hydroxide and of Hydrogen Peroxide on Cholesterol.*" (Preliminary Note). By Robert Howson Pickard and Joseph Yates.

Cholesterol is slowly decomposed by prolonged fusion with potassium hydroxide. From the products of the decomposition, small quantities of two crystalline acids have been isolated. The *acid*, $C_{26}H_{44}(OH)\cdot CO_2H$, melts at 241°, is optically active, and forms an *acetyl* derivative (m. p. 163°) and an *ethyl* ester (m. p. 62°). The *acid*, $C_{24}H_{42}(CO_2H)_2$, melts at 190°, and forms an amorphous *silver* salt.

Cholesterol or its acetate is also rapidly attacked by hydrogen peroxide, which is employed to the best advantage under the conditions described by W. H. Perkin, jun., (*Proc.*, 1907, xxiii., 166). The main product is a neutral *substance*, $C_{27}H_{46}$(or $_{48}$)O_3, m.p. 239°, which is probably isomeric with dehydrocholestantriol (Windaus, *Ber.*, 1907, xl., 257). The *monoacetate* melts at 212°, the *diacetate* at 165°, and the *dipropionate* at 172°. It may be oxidised to a *keto-alcohol*, $C_{27}H_{44}O_3$ (m. p. 232°), which forms a *monoacetate*, m. p. 233°, and a *phenylhydrazone*, m. p. 164°. The substances melting at 239° and 232° contain the hydroxyl group of cholesterol, and are readily oxidised to the diketo-alcohol ("oxycholestendiol") described by Mauthner and Suida (*Monatsh.*, 1896, xvii., 590). Dicholesteryl ether behaves in an analogous manner with hydrogen peroxide, forming a neutral *substance*, $(C_{27}H_{45}O_2)_2O$(?), which melts at 192° and forms a *diacetate*, m. p. 143°. The formation of these substances appears to confirm the deductions of Windaus (see summary in *Arch. Pharm.*, 1908, ccxlvi., 117) as to the relation between the constitution of cholesterol and that of some of the products of its oxidation by permanganic and chromic acids.

101. "*The Volumetric Estimation of Silver.*" By William Robert Lang and J. C. Woodhouse.

The apparatus employed for the estimation of sulphates and salts of barium (*Trans.*, 1907, xci., 1370) was found unsuitable for the determination of silver, owing to the slowness with which the milky solution in the thin tube cleared. Some filtering medium appeared necessary, so, after several unsuccessful attempts with glass-wool and with asbestos, clean sand was used, held in position by a glass-wool plug in a curved tube. The packed sand filter necessitated the use of a filter-pump for washing, and was found a great convenience. Experiments were made with solutions containing a known amount (0·5 grm.) of silver, to which an excess of N/10 sodium chloride was added and the excess titrated with N/10 silver nitrate. Each titration occupied about half-an-hour, and the mean error of six determinations was 0·286 per cent. On using 1 grm. of silver, 100 cc. of N/10 sodium chloride, and titrating back with N/100 silver nitrate, the error was reduced to 0·198 per cent. The effect of free nitric acid in varying amounts on the estimation was also tried and found to reduce the error still further, as low as 0·063 per cent. The method and apparatus were then employed to determine silver in

bullion under the same conditions as obtained in the Gay-Lussac method, namely, 1 grm. of silver in nitric acid, 100 cc. of N/10 sodium chloride, and finishing with N/100 silver nitrate. The result of seven estimations done in this way, each occupying about half-an-hour, gave a mean error of 0·067 per cent. It seems reasonable to hope that this apparatus may prove of use to those requiring a rapid and accurate method of estimating silver.

102. "*A Criticism of Werner's Theory, and the Constitution of Complex Salts.*" By John Albert Newton Friend.

The author pointed out the disadvantages of Werner's theory, as applied to simple and complex salts, and suggested new structural formulæ which are free from these objections.

103. "*The Action between Potassium Sulphite and Potassium Pentathionate.*" By Edward Divers.

Debus published, in 1888, a paper on the polythionic acids (*Trans.*, liii., 278), which is still a classic on the subject, but can remain so only so long as later researches leave its accuracy in all essentials untouched. It is therefore important to point out that the accuracy of Debus' investigation of the action between a sulphite and a pentathionate is not affected by Colefax's quite recent work (*Trans.*, 1908, xciii., 798), as it would appear to be from pp. 803—804 of that author's paper. Debus is in agreement with Colefax, but his work is more comprehensive than Colefax's and with a wider object in view.

Colefax has found that potassium sulphite in solution is, nearly all, rapidly converted by potassium pentathionate into the thiosulphate, whilst Debus has stated (*loc. cit.*, p. 344) that "potassic sulphite and potassic pentathionate form potassic thiosulphate and potassic trithionate." The latter author's experimental proof of this is given on p. 332, but in an irregular form, for, instead of using potassium sulphite, he dissolved the potassium pentathionate in a concentrated solution of sulphur dioxide and then added barium carbonate. He gives two chemical equations in explanation of this procedure, which are equivalent to $K_2S_5O_6 + 2K_2SO_3 = K_2S_3O_6 + 2K_2S_2O_3$, an equation indicating a 50 per cent fall in iodine titration-value, in accordance with Colefax's observations. By using barium carbonate, Debus accomplished an easy separation of the products, obtaining the thiosulphate as insoluble barium salt, and the trithionate as potassium salt, in crystals. Colefax worked throughout his investigations on molecular proportions of his salts, as was proper for the end he had in view, but the addition to the above equation of a second molecule of pentathionate is without effect on the action it expresses or on the iodine value. Working quantitatively, and with the actual salts, Colefax has made, it should be added, a real addition to our knowledge of the reaction.

Debus did experiment with potassium sulphite itself, converting it into thiosulphate by the pentathionate, but he employed solutions a hundred times stronger than those used by Colefax, with the result, not met with by the latter, that he also obtained much sulphur dioxide. His explanation of this evolution of sulphur dioxide is a suggestion of deep theoretical significance, if well founded, with apparently no other explanation possible in place of it. His experiment has no bearing on Colefax's investigation with highly dilute solutions, and Debus's explanation of it is certainly quite inapplicable to the results obtained in other ways, both by himself and by Colefax, as the latter has rightly pointed out in connection with his own work.

104. "*Note on Phenolic Thetines and their Action with Benzoyl Chloride.*" By Edward de Barry Barnett and Samuel Smiles.

When phenol and phenetole *p*-sulphoxide are dissolved in concentrated sulphuric acid, *phenoxydiphenetylsulphonium sulphate* is formed. The *platinichloride* of the base is an orange-brown powder melting at 123—125°. The condensation of diphenyl sulphoxide with phenol does not take place in cold sulphuric acid, but it may readily be effected by warming with phosphoric oxide. *Phenoxydiphenylsulphonium platinichloride* occurs in orange crystals, which rapidly decompose at about 210°. The salts of these bases are colourless, viscous oils. On treatment with aqueous alkali hydroxide, they yield the phenolic thetines. These are unstable, yellow oils, which are soluble in water or chloroform and insoluble in concentrated aqueous alkali hydroxide. They are formed (by elimination of alkali salt) from the sodium salt of the sulphonium base—

$$(C_6H_5)_2(C_6H_4\cdot ONa)SCl = NaCl + (C_6H_5)_2{:}S\cdot C_6H_4\cdot O.$$

With benzoyl chloride in aqueous alkaline solution, the phenolic thetines yield benzoic anhydride, and in this respect they resemble certain tertiary nitrogen bases, for example, pyridine (Minunni, *Gazzetta*, 1892, xxii., 215). With hydrochloric acid they furnish the chlorides of the corresponding sulphonium bases.

105. "*The Relation between Dielectric Constant and Chemical Constitution.* Part I. *Stereoisomeric Compounds.*" By Alfred Walter Stewart.

The author has examined active and racemic compounds and also geometrical isomerides, and finds that the influence of the spacial arrangement of atoms on the dielectric constants of isomeric substances is not clearly marked. A difference in electric absorption was noticed in one case, the active isomeride having a stronger absorptive power than the racemic form.

106. "*An Apparatus for Determining the Specific Inductive Capacity of Organic Liquids.*" By Alfred Walter Stewart.

In this apparatus, Hertzian waves are generated and conducted along a secondary circuit in the usual manner. The secondary circuit is led through a vertical graduated tube, and an adjustable bridge between the wires of the circuit is obtained by moving mercury up and down within the tube. The apparatus is calibrated in the usual way, by means of liquids of known specific inductive capacity. The chief advantages over the previous method (Drude, *Zeit. Phys. Chem.*, 1897, xxiii., 267) lie in the regulation of temperature by jacketing the tube (which could not be done easily in the Drude apparatus), in the sharpness of contact between the mercury and the wires of the secondary circuit, and in the comparatively small quantity of substance required for the new apparatus. Reduced pressures can also be used.

107. "*The Influence of Solvents on the Rotation of Optically Active Compounds.* Part XII. *Ethyl Tartrate in Aromatic Halogen Derivatives.*" By Thomas Stewart Patterson and David Paterson McDonald.

The rotation of ethyl tartrate has been examined in chlorobenzene, bromobenzene, iodobenzene, *p*-dichlorobenzene, and *a*-bromonaphthalene. The data were compared with others formerly obtained for benzene and for various aliphatic halogen derivatives. The relationship between rotation and molecular solution-volume in these solvents was discussed, as was also the influence of temperature change on the rotation of dilute solutions of ethyl tartrate in *a*-bromonaphthalene.

108. "*A New Test for Silver.*" By Arnold William Gregory.

When a solution of a silver salt is added to a mixture of 20 cc. of aqueous ammonium salicylate (20 grms. of salicylic acid neutralised with ammonium hydroxide, a slight excess of the latter added, and the solution made up to 1 litre), and 20 cc. of ammonium persulphate solution (50 grms. in 1 litre), an intense brown colour is produced. By this reaction, 0·01 milligrm. of silver can be detected. As lead does not give this reaction, silver may be tested for in presence of this element; 1·1 milligrm. of silver may be detected in this manner in the presence of 0·2 grm. of lead.

It was found that the brown substance formed in this reaction does not contain silver, and it is probable that the silver salt acts as a catalyst, since on boiling a solution of ammonium salicylate with ammonium persulphate a similar brown colour is produced.

109. "*The Spontaneous Crystallisation of Substances which form a Continuous Series of Mixed Crystals: Mixtures of Naphthalene and β-Naphthol.*" By Henry Alexander Miers and Florence Isaac.

The object of this research was to ascertain whether there are definite temperatures of spontaneous crystallisation in mixtures which yield a continuous series of mixed crystals.

By means of experiments on mixtures of naphthalene and β-naphthol of known composition contained in sealed tubes, the authors have determined the supersolubility curve, and also the freezing-point curve and the melting-point curve for the whole series of mixtures.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 14, April 6, 1908.

Isomer of Diphenylcamphomethane.—A. Haller and E. Bauer.—Diphenylcamphomethane, which fuses at 106°, can be transformed into an isomer fusing at 136° to 137°. When the product of the reaction between phenyl magnesium bromide and benzylidene camphor is treated with benzyl chloride, a benzoate of diphenylcamphomethane is formed. This benzoate on saponification yields benzoic acid, and the same diphenylcamphomethane, fusing at 136—137°, as that resulting from the transformation of the isomer fusing at 106°. The authors have not as yet succeeded in determining the relation of the two compounds to one another.

Presence of Spark Lines in the Arc Spectrum.—Ch. Fabry and H. Buisson.—When the spark and arc spectra of a metal are compared it is found that certain lines belonging to the second are absent from the first or appear only very faintly. These lines are called spark lines (Lockyer's enhanced lines). The authors have discovered that in the spectrum of iron all the spark lines are emitted by certain parts of the arc. The arc appears to the eye to be formed of two flames which originate from a point situated on the drop of molten iron at the end of each electrode. These points emit all the spark lines, while the arc flames do not show them. The nickel and cobalt arcs exhibit the same phenomenon.

New Method of Determining Mercury Vapour in Air.—P. Ménière.—The method depends upon the preparation of intimate mixtures of the air containing mercury with the vapours of boiling nitric acid. The whole of the metal is thus fixed as nitrate, and can be determined colorimetrically by means of diphenylcarbazide. The apparatus for preparing the mercury nitrate consists of a 1500 cc. bulb furnished with two openings. Through the first is passed a tube for introducing the gas, while the second is connected with a Lebel-Schlœsing spiral. This apparatus is connected with a second, exactly like it to avoid loss. Nitric acid is placed in each bulb, and is boiled, while the air containing mercury is passed in. The nitrate solution thus obtained is slowly evaporated, and the mercury determined by Cazeneuve's method with diphenylcarbazide.

Combustion of Gases by Incandescence in presence of Oxidisable and Incombustible Substances.—Jean Meunier.—Incandescent substances localise combustion at their surface, and the experimental results are different according as the incandescent substance is oxidisable or incombustible. At ordinary temperatures the chemical affinity of oxygen for hydrogen, carbon, and their compounds is not revealed in gaseous mixtures. At the temperature of ignition, however, an attraction is exercised suddenly and violently between the molecules of the combustible substance and those of the oxygen. The chemical attraction is generally accompanied by a physical attraction. This is clearly shown when a combustible solid having given up all its volatile matter continues to burn without a flame. The molecules of oxygen are evidently attracted by those of the burning solid, when the latter is at a sufficiently high temperature. The author has illustrated this phenomenon by igniting piano-wire in oxygen and finding the increase of weight, which shows that some oxygen was attracted from a distance to the burning wire. The intensity of incandescence does not depend only upon the nature of the substance, but also upon the composition of the combustible mixture which surrounds it.

Variations in the Composition of Ammonium Phosphomolybdate.—G. Chesneau.—The amount of phosphorus in precipitates of ammonium phosphomolybdate appears to vary with the concentration of the phosphoric and molybdic acids and of the ammoniacal salts. If, however, Carnot's method of double precipitation is adopted, precipitates of perfectly constant composition are obtained, provided that—(1) 50 cc. of freshly prepared molybdic reagent and 5 grms. of ammonium nitrate are employed per grm. of metal; (2) the first precipitation is performed between 65° and 70°, and thus no ammonium tetramolybdate is formed; (3) the precipitate is always dissolved in the same quantity of ammonia. After re-acidifying with concentrated nitric acid the precipitate must be allowed to settle, and 15 cc. of the molybdic reagent added. The whole must be kept for two hours at 40°, and the precipitate washed with pure water.

Ammoniacal Chlorides of Dimercurammonium.—H. Gaudechon.—The study of the reactions and the thermochemistry of the two compounds, $(NHg_2Cl)_2H_2O$ and $NHg_2Cl.H_2O$, shows that two derivatives, $(NHg_2Cl)_2.NH_3$ and $NHg_2Cl.NH_3$, correspond to these compounds, the water molecule being replaced by the ammonia molecule. Thus the group NHg_2Cl, which has not yet been isolated, behaves like a true metallic chloride. Rammelsberg's compound, $NHg_2Cl.NH_4Cl$, may be regarded as the chlorhydrate of the complex ammonium base.

Arbutine and some of its Derivatives.—Em. Bourquelot and H. Hérissey.—Arbutine, $C_6H_4{<}^{OC_6H_{15}O_5}_{OH}$, and its methyl, benzyl, and dinitro derivatives, can be hydrolysed by emulsine. They are all derived from *d*-glucose, and are lævorotatory, and thus follow the general rules enunciated by the authors.

Comparative Study of the Dehydration of Atrolactic and *p*-Methoxyatrolactic Acids.—J. Bougault.—Atrolactic acid, or rather its ethyl ether, is dehydrated by prolonged boiling with hydrochloric acid (3 parts acid to 1 part water). It gives atropic acid and some of Fittig's isatropic acid. In the cold it yields β-chlorhydratropic acid, $C_6H_5—CH(CH_2Cl)—CO_2H$, and a little isatropic acid. When atrolactic acid is boiled with acetic acid or dilute mineral acid (10 per cent), no appreciable quantities of atropic acid are formed. *p*-Methoxyatrolactic acid is dehydrated much more readily. When boiled with acetic acid or dilute mineral acids, it gives good yields of *p*-methoxyatropic acid. With concentrated hydrochloric acid a new acid is formed by the condensation of two molecules of *p*-methoxyatropic acid. The author calls it di-*p*-methoxyatropic acid, $(C_{10}H_{10}O_3)_2$.

Formation of Mixtures of Isomers of Constant Melting-point in Friedel and Craft's Reaction.—G. Perrier and H. Caille.—When phenylnaphthylketone is

prepared by Friedel and Craft's method after decomposing with water a product is obtained which melts sharply at 54°. This is neither the α-derivative (melting-point 75°) nor the β derivative (melting-point 82°). It can be separated into these isomers by crystallisation in ligroin and mechanical separation of the crystals, or by Rousset's method (formation in benzene of the insoluble β-picric derivative to the exclusion of the α-derivative). It appears to be a simple mechanical mixture which, like mixtures of salts or alloys, melts at a lower temperature than its constituents.

No. 15, April 13, 1908.

Action of Heat on the Hydrates of Lithium Hydroxide.—M. de Forcrand.—The evaporation of a concentrated solution of the pure hydroxide in cold pure air gives the compound $LiOH.H_2O$, which yields LiOH in a vacuum at the ordinary temperature. By heating the commercial hydroxide in a current of dry hydrogen it fuses at 445°, losing water. Its weight becomes absolutely constant at that temperature, and its composition is $LiOH + .125H_2O$. This is undoubtedly a definite compound; it can be heated for hours in a current of hydrogen without losing weight. After heating for eight to ten hours to 660° and 1 two hours to 780°, the anhydrous oxide, Li_2O, or rather nLi_2O, is obtained.

Sulphur Compounds of Thorium.—A. Duboin.—The author prepared thorium chloride by passing a current of chlorine containing carbon tetrachloride over thorium hydroxide heated in a glass tube. The chloride thus obtained always contains a little oxychloride. Sulphuretted hydrogen begins to react on it at a dull red heat, and gives a dark brown amorphous product. In a porcelain tube at a red heat a very few crystals are obtained with amorphous brown and yellow products. If the chloride of thorium, to which an excess of sodium chloride has been added, is placed in a porcelain boat in the middle of a porcelain tube and heated in a reverberatory furnace, and a current of dry sulphuretted hydrogen is passed in, on cooling and extracting with water it is seen that the greater part of the product consists of brown micaceous shining lamellæ. These can be separated by sifting from the amorphous product, and small quantities of yellow crystals also formed. The yellow crystals can also be isolated by treating the sifted part with nitric acid, when the brown substance is attacked rapidly, and the yellow crystals much more slowly. The brown substance is thorium sulphide, ThS_2, whilst the yellow crystals are an oxysulphide.

Semicatalysis. Oxidation of Hydrocarbons in presence of Phosphorus.—Albert Colson.—When phosphorus is dissolved in terebenthene in presence of air the liquid becomes turbid, and a white curdy or colloidal deposit is formed. It is odorous, is insoluble in water, but soluble in ether and acetic acid. It does not contain free phosphoric acid. When the ethereal solution is dried in air a resinous substance of composition $PO_4H_3(C_{10}H_{16}O_3)_2$ is obtained. It is evident that the terebenthene has been oxidised, and since it does not oxidise in absence of phosphorus the phenomenon may be regarded as a sort of catalysis. Since, on the other hand, the phosphorus itself undergoes an alteration it is not a true catalytic action, but one which the author designates semi-catalysis.

Alloys of Platinum and Thallium.—L. Hackspill.—Platinum sponge dissolves readily in fused thallium, giving an alloy the melting-point of which is lower than that of pure thallium when the amount of platinum does not exceed 10 per cent. When more platinum is added the melting-point is first lowered, and then rapidly raised, reaching 855°, when 65 per cent of platinum is present. All these alloys are very brittle. The alloys rich in thallium contain white shining crystals, the number and dimensions of the crystals being at a maximum in the alloy, PtTl. This compound closely resembles PtPb.

Austenite.—Ed. Maurer.—The author has investigated the preparation of austenite from steel containing a little nickel and manganese and comparatively large amounts of carbon. Taking three specimens of the following composition—

	I.	II.	III.
Nickel	3·73	—	—
Manganese ..	—	1·83	2·20
Carbon	1·21	1·18	1·94
Silicon	0·28	0·88	0·94

he heated them for fifteen minutes to 1050°, and then tempered them in ice water. The two first specimens gave martensite and the third pure austenite.

No. 16, April 21, 1908.

Reducing Power of Ferropyrophosphates. — P. Pascal.—Concentrated and dilute solutions of ferropyrophosphates instantly reduce salts of gold and silver in the cold, but have no effect upon platinum salts even at 100°. Alkaline ferropyrophosphates reduce a solution of mercuric chloride, giving, first, mercurous chloride and then mercury. They precipitate cuprous iodide or bromide from copper salts on addition of alkaline iodide or bromide.

MEETINGS FOR THE WEEK.

MONDAY, June 1st.—Royal Institution, 5. General Monthly Meeting.
——— Society of Chemical Industry, 8. "The 'Autolysator,' an Apparatus for the Automatic Estimation of Carbon Dioxide," by C. A. Keane and H. Burrows. "Some Modern Chemical Plant" and "Explosions and the Building of Explosive Factories," by O. Guttmann. "Estimation of Orcinol in Orchella Weed," by H. E. Watt.

TUESDAY, 2nd.—Royal Institution, 3. "Animal Heat and Allied Phenomena," by Prof. William Stirling, M.D.

WEDNESDAY, 3rd.—Society of Public Analysts, 8. "Studies in Steam Distillation—Part III., The Fatty Acids," by H. D. Richmond. "Detection of Poisonous Metals," by G. D. Lander and H. W. Winter. "Estimation of Cocoanut Oil in Butter," by R. Ross. "Ochoco Fat," by J. Lewkowitsch. "Detection of Small Quantities of Methyl Alcohol in the presence of Ethyl Alcohol," by L. E. Hinkel. "Separation of certain Volatile Fatty Acids by Extraction with Benzene or Toluene," by T. R. Hodgson.

THURSDAY, 4th.—Royal Institution, 3. "The Chemistry of Photography" by Alexander Scott, F.R.S., &c.
—— Chemical, 8.30. "Condensation Products from Pinene Aminodicarboxylic Acid," by W. Godden. "A Delicate Test for Bromides alone or in Solution with Chlorides," by J. S. Jamieson. "Experiments on the Synthesis of 1-Methylcyclohexylidene-4-acetic Acid," by W. H. Perkin and W. J. Pope. "The Triazo-group—Part IV., Allyl Azoimide," by M. O. Forster and H. E. Fierz.

FRIDAY, 5th.—Royal Institution, 9. "The Nadir of Temperature and Allied Problems," by Prof. Sir James Dewar, F.R.S.

SATURDAY, 6th.—Royal Institution, 3. "The Art of Bach and Future Developments," by H. Walford Davies, Mus.Doc.

INSTRUCTION IN

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Manuals: Alfred Jörgensen, "Micro-organisms and Fermentation" (London and New York, Macmillan & Co., 1900); and "The Practical Management of Pure Yeast" (London, "The Brewing Trade Review," 1903).

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THE CHEMICAL NEWS.

Vol. XCVII., No. 2532.

SOME OF THE NON-METALLIC ELEMENTS IN CONNECTION WITH VALENCY AND SPECIFIC GRAVITY.

By GEO. WOODIWISS.

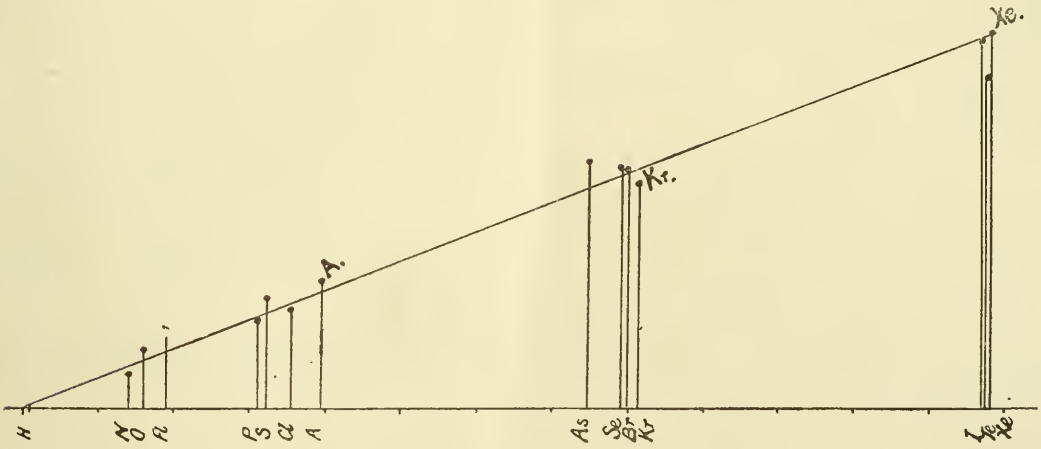
It will probably readily be granted that one of the most interesting studies in chemistry is that of periodicity. What may possibly not be so evident is the order of the elements in the periods, different writers giving different versions of the matter. To the scientist with a full grasp of the whole subject this may be of little moment, but to the student with no desire for making this a speciality it is quite another thing. From one writer he may learn that lithium, sodium, copper, &c., follow each other in a natural grouping of the elements, casually from another he finds that lithium, potassium, &c., is considered to be more correct, and incidentally he may find that for their own purpose neither of the writers will adopt either of the orders given, but that each will place lithium, sodium, potassium, &c., in a group of alkali metals with copper altogether separate. The average student thus fails to appreciate the full importance of periodicity, and passes it by as a mere curiosity.

Again, he may be taught that there is a systematic change in valency progressing regularly from 1 to 8, after which there is a sudden drop to 0 for the argon group. The question will naturally arise, is the argon group by this method placed in a correct position? We find on taking a list of the elements in the order of atomic weight that this group as a rule falls between the alkali metals and the halogens, both of which are monovalent; and as valency has systematically decreased from either direction to this point, both with and against atomic weight, it is to be expected that it will further decrease and that for the argon group it will be of a value of less than 1. But are we justified in placing this amount definitely at 0? By so doing are we not giving a value to an unknown quantity, and precluding even the possibility of any element with a valency of a fraction of 1? Indirectly we may obtain evidence that it is not absolutely outside the bounds of possibility for such a valency to be, the indication pointing to this group possibly having a value of 0·5. No chemical action is known to take place with an exchange value of less than 1, consequently there would be no inconsistency if the above actually was the correct figure.

In support of this, if we take a list of the elements in the order of the atomic weight, we find that immediately preceding the argon group are the triads, diads, and monads of the non-metallic class, a characterising feature of which is the specific gravity being approximately directly proportionate to the atomic weight, as distinguished from the adjoining metals of similar valency (see Chemical News, xcvii., p. 122). A second feature is, the specific gravity of the groups vary, approximately, as the square root of the valency value. This singular connection between valency and specific gravity is only applicable to the argon group by adopting a value of 0·5.

In each case in the following lists the first set of figures is the specific gravity taken, and the last set is specific gravity divided by the square root of the valency value.

				Fl	1·1	÷ $\sqrt{1}$	= 1·1
A	1·21	÷ $\sqrt{0·5}$	= 1·7	Cl	1·33	,,	1·3
Kr	2·15	,,	3·0	Br	3·18	,,	3·2
Xe	3·52	,,	5·0	I	4·95	,,	4·9
O	1·13	÷ $\sqrt{2}$	= 0·8	N	0·88	÷ $\sqrt{3}$	= 0·5
S	2·07	,,	1·5	P	2·1	,,	1·2
Se	4·50	,,	3·2	As	5·7	,,	3·3
Te	6·23	,,	4·4	Sb = metallic.			



To show the connection more clearly the accompanying diagram is constructed, wherein the quotient of specific gravity, divided by square root of assumed valency value, is plotted against atomic weight. Here we see the inert elements argon, krypton, and xenon with an assumed valency of 0·5 behaving in accord with others of the non-metallic class.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 1st instant, the Duke of Northumberland, K.G., President, in the Chair. Mr. Franklin Adams, the Right Hon. the Duke of Devonshire, Dr. W. Heptinstall Millar, Lady Martin, Mr. P. Mavrogordato, and Mr. J. Ziffo were elected Members. The Chairman announced that he had nominated the following gentlemen as Vice-Presidents for the ensuing year;—The Right Hon. the Earl of Halsbury, Dr. Donald W. C. Hood, Dr. Ludwig Mond, the Right Hon. the Earl of Rosse, Mr. Alexander Siemens, The Right Hon. Sir James Stirling, Sir James Crichton-Browne (Treasurer), and Sir William Crookes (Honorary Secretary).

ON THE CALCULATION OF THERMO-CHEMICAL CONSTANTS.

IV.—THERMAL CONSTANTS OF ORGANIC OXYGEN COMPOUNDS (*continued*).

By H. STANLEY REDGROVE, B.Sc. (Lond.), F.C.S.

(Concluded from p. 255).

5. *Molecular Heats of Combustion of Ketones and Aldehydes.*

ALL ketones and aldehydes can theoretically be obtained by replacing $2e$ hydrogen atoms in the corresponding hydrocarbon by e oxygen atoms each "doubly linked" to carbon, where e is some integer; the following constant will therefore be required:—

ω_2 = the algebraic sum of the following heats—(i.) due to the severance of two C.H links; (ii.) due to the combustion of two hydrogen atoms (to liquid water), minus the algebraic sum of the following heats—(iii.) due to the severance of a C:O link; (iv.) one-half that due to the formation of an oxygen molecule; or as it can be more simply written:—

ω_2 = the sum of the following heats—(ii.) due to the combustion of two hydrogen atoms (to liquid water); (iii.) due to the formation of a C:O link, minus the sum of the following heats—(i.) due to the formation of two C.H links; (iv.) one-half that due to the formation of an oxygen molecule.

So that the general ketone and aldehyde,—

$$nC+2(n+1-a-2b-p-e)H+ +(n+p-a-b-1)L_1+aL_2+bL_3+cO+e(C{:}O)\text{ links},$$

can be written—

$$nC+2(n+1-a-2b-p)H+ +(n+p-a-b-1)L_1+aL_2+bL_3-e\omega_2 =n\alpha-(n+p-a-b-1)\beta-a\gamma-b\delta-e\omega_2.$$

The value of ω_2 can be shown from a consideration of carbon dioxide to be identical with that of $\frac{\alpha}{2}$ in either of the following ways:—

1. α = molecular heat of combustion of methane (to gaseous carbon dioxide and liquid water) = the algebraic sum of the following heats—(i.) due to the combustion of one carbon atom; (ii.) due to the severance of four C.H links; (iii.) due to the combustion of four hydrogen atoms (to liquid water). But as carbon on combustion gives O:C:O, the heat of combustion of one carbon atom = the heat due to the formation of two C:O links, less the heat due to the formation of an oxygen molecule.

Therefore α = the sum of the following heats—(iii.) due to the combustion of four hydrogen atoms (to liquid water); (i.) due to the formation of two C:O links, minus the sum of the following heats—(ii.) due to the formation of four C.H links; (i.) due to the formation of an oxygen molecule.

Therefore $\alpha = 2\omega_2$, whence $\omega_2 = \frac{\alpha}{2} = 105{\cdot}4$ cals.

2. Otherwise, CO_2 can be written $\alpha-2\omega_2$; its heat of combustion is zero, whence $\alpha-2\omega_2=0$, so that $\omega_2 = \frac{\alpha}{2} = 105{\cdot}4$ cals. as before.

This value of ω_2, as will be shown later, is in excellent agreement with the values obtained for the carbonyl oxygen in certain acids and esters.

In Table III. will be found the molecular heats of combustion, corrected for constant volume, of three aldehydes and two ketones given by Thomsen. These give lower values for ω_2, thus:—

Acetaldehyde is $CH_3.CHO$; *i.e.*, $2\alpha-\beta-\omega_2$ M.H.C. found = 281·0 cals. Therefore $\omega_2 = 2\alpha-\beta-281{\cdot}0$ cals. = (421·6 − 52·5 − 281·0 cals.) = 88·1 cals.

The values of ω_2 calculated thus from each aldehyde and ketone are given in the table. The mean value for the aldehydes is $\omega_2 = 87{\cdot}7$ cals., for the ketones $\omega_2 = 91{\cdot}4$ cals.; using these values the molecular heats of combustion of all the aldehydes and ketones given have been calculated, and are exhibited together with the differences between them and the experimental, and the percentage errors in Table III. The agreement is excellent.

It must, however, be noticed that probably the above two latter values are not the true values of ω_2, but are purely empirical, inasmuch that it seems very probable that all (or at least many) ketones and aldehydes are, under ordinary circumstances, mixtures of true carbonyl-oxygen compounds—the true ketones and aldehydes, and unsaturated secondary alcohols (*i.e.*, mixtures of the keto and enol forms); these latter it is worth while noticing have theoretically relatively high molecular heats of combustion.

6. *Molecular Heats of Formation of Aldehydes and Ketones.*

The molecular heat of formation constant corresponding to ω_2 is:—

ω_2' = the algebraic sum of the following heats—(i.) due to the decomposition of a hydrogen molecule; (ii.) due to the formation of two C.H links, minus the algebraic sum of the following heats—(iii.) one-half that due to the decomposition of an oxygen molecule; (iv.) due to the formation of a C:O link, or as it can be more simply written:—

ω_2' = the sum of the following heats—(ii.) due to the formation of two C.H links; (iii.) one-half that due to the formation of an oxygen molecule, minus the sum of the following heats—(i.) due to the formation of a hydrogen molecule; (iv.) due to the formation of a C:O link.

Therefore, $\omega_2+\omega_2'$ = the heat due to the combustion of two hydrogen atoms (to liquid water) less the heat due to the formation of a hydrogen molecule = the molecular heat of combustion of molecule hydrogen to liquid water = 67·5 cals.; whence $\omega_2' = 67{\cdot}5$ cals. $-\omega_2$.

Therefore ω_2' (CO_2, acids and esters; see hereinafter) = (67·5 − 105·4) cals. = −37·9 cals. ω_2' (aldehydes) = (67·5 − 87·7) cals. = −20·2 cals. ω_2' (ketones) = (67·5 − 91·4) cals. = −23·9 cals.

In Table III. will be found the molecular heats of formation (at constant volume) of the ketones and aldehydes given by Thomsen, from which the following values of ω_2' have been calculated in a similar manner as were those of ω_2:—

ω_2' (aldehydes) = −20·1 cals. ω_2' (ketones) = −23·55 cals.

Using the mean values ω_2' (aldehydes) = −20·2 cals., ω_2' (ketones) = −23·7 cals.; the molecular heats of formation of all the aldehydes and ketones given have been calculated, and are exhibited together with the differences between them and and the experimental in Table III.

7. *Molecular Heats of Combustion of Esters.*

The general formula for all esters derived from monobasic carboxy acids and mono-hydroxy alcohols is:—

$$nC+2(n-a-2b-p-1)H+(n+p-a-b-1) L_1+aL_2+bL_3+2O+1(C{:}O)\text{ link}+2(C{.}O)\text{ links}^* =nC+2(n+1-a-2b-p)H+ +(n+p-a-b-1)L_1+aL_2+bL_3-\omega-\omega_2, =n\alpha-(n+p-a-b-1)\beta-a\gamma-b\delta-\omega-\omega_2.$$

In Table IV. will be found the molecular heats of combustion (corrected for constant volume) of nine such esters given by Thomsen; from these the value of $\omega+\omega_2$ has been calculated, thus:—

Methyl formate is $H{\cdot}C\overset{O}{\underset{OCH_3}{<}}$; *i.e.*, $2\alpha-\omega-\omega_2$.

M.H.C. found = 240·6 cals.

Therefore $\omega+\omega_2 = 2\alpha-240{\cdot}6$ cals. = (421·6 − 240·6) cals. = 181·0 cals.

* For common esters put $p=-1$.

TABLE III.—Aldehydes and Ketones.

1. Substance.	2. Formula.	Molecular Heat of Combustion. 3. Formula.	4. M.H.C. found (Thomsen) constant vol. Cals.	5. ω_2 Calculated. Cals.	6. M.H.C. calculated. Cals.	7. Difference between cols. 4 and 6. Cals.	8. Error. Per cent.	Molecular Heat of Formation. 9. Formula.	10. M.H.F. (Thomsen) constant vol. Cals.	11. ω_2' Calculated. Cals.	12. M.H.F. calculated. Cals.	13. Difference between cols. 10 and 12. Cals.
Aldehydes—												
Acetic aldehyde ..	$CH_3.CHO$	$2\alpha-\beta-\omega_2$	281·0	88·1	281·4	+0·4	+0·14	$2\alpha'-\beta'-\omega_2'$	47·9	−20·5	47·6	−0·3
Propionic aldehyde .	$C_2H_5.CHO$	$3\alpha-2\beta-\omega_2$	439·6	87·8	439·7	+0·1	+0·02	$3\alpha'-2\beta'-\omega_2'$	53·8	−20·2	53·8	0·0
Isobutyric aldehyde.	$C_3H_7.CHO$	$4\alpha-3\beta-\omega_2$	598·4	87·3	598·0	−0·4	−0·07	$4\alpha'-3\beta'-\omega_2'$	59·3	−19·5	60·0	+0·7
		Mean .. .. ω_2 =		87·7				Mean .. .. ω_2' =		−20·1		
Ketones—												
Dimethyl ketone ..	$(CH_3)_2CO$	$3\alpha-2\beta-\omega_2$	436·1	91·3	436·0	−0·1	−0·02	$3\alpha'-2\beta'-\omega_2'$	57·3	−23·7	57·3	0·0
Methylpropyl ketone	$CH_3.CO.C_3H_7$	$5\alpha-4\beta-\omega_2$	732·5	91·5	752·6	+0·1	+0·01	$5\alpha'-4\beta'-\omega_2'$	69·4	−23·4	69·7	+0·3
		Mean .. .. ω_2 =		91·4				Mean .. .. ω_2' =		−23·55		

TABLE IV.—Esters.

			$\omega+\omega_2$ calculated.					$\omega'+\omega_2'$ calculated.			
Esters—											
Methyl formate ..	$H.CO_2CH_3$	$2\alpha-\omega-\omega_2$; $1\frac{1}{2}\alpha-\omega$	240·6	181·0	240·8	+0·2	+0·08	$2\alpha'-\omega'-\omega_2'$	88·3	−45·9	88·1	−0·2
Methyl acetate ..	$CH_3.CO_2CH_3$	$3\alpha-\beta-\omega-\omega_2$; $2\frac{1}{2}\alpha-\beta-\omega$	398·4	181·5	399·1	+0·7	+0·18	$3\alpha'-\beta'-\omega'-\omega_2'$	95·0	−46·4	94·3	−0·7
Methyl propionate	$C_2H_5.CO_2CH_3$	$4\alpha-2\beta-\omega-\omega_2$; $3\frac{1}{2}\alpha-2\beta-\omega$	552·8	185·4	557·4	+4·6	+0·83	$4\alpha'-2\beta'-\omega'-\omega_2'$	105·0	−50·2	100·5	−4·5
Methyl isobutyrate	$C_3H_7CO_2CH_3$	$5\alpha-3\beta-\omega-\omega_2$; $4\frac{1}{2}\alpha-3\beta-\omega$	715·5	181·0	715·7	+0·2	+0·03	$5\alpha'-3\beta'-\omega'-\omega_2'$	106·8	−45·8	106·7	−0·1
Ethyl formate ..	$H.CO_2C_2H_5$	$3\alpha-\beta-\omega-\omega_2$; $2\frac{1}{2}\alpha-\beta-\omega$	399·2	180·7	399·1	−0·1	−0·03	$3\alpha'-\beta'-\omega'-\omega_2'$	94·2	−45·6	94·3	+0·1
Ethyl acetate ..	$CH_3.CO_2C_2H_5$	$4\alpha-2\beta-\omega-\omega_2$; $3\frac{1}{2}\alpha-2\beta-\omega$	545·4	(192·8)	557·4	+12·0	+2·20	$4\alpha'-2\beta'-\omega'-\omega_2'$	112·4	(−57·6)	100·5	−11·9
Propyl formate ..	$H.CO_2C_3H_7$	$4\alpha-2\beta-\omega-\omega_2$; $3\frac{1}{2}\alpha-2\beta-\omega$	557·6	180·6	557·4	−0·2	−0·04	$4\alpha'-2\beta'-\omega'-\omega_2'$	100·2	−45·4	100·5	+0·3
Isobutyl formate .	$H.CO_2C_4H_9$	$5\alpha-3\beta-\omega-\omega_2$; $4\frac{1}{2}\alpha-3\beta-\omega$	718·4	178·1	715·7	−2·7	−0·35	$5\alpha'-3\beta'-\omega'-\omega_2'$	103·8	−42·8	106·7	+2·9
Allyl formate ..	$H.CO_2C_3H_5$	$4\alpha-\beta-\gamma-\omega-\omega_2$; $3\frac{1}{2}\alpha-\beta-\gamma-\omega$	527·0	(174·7)	520·9	−6·1	−1·16	$4\alpha'-\beta'-\gamma'-\omega'-\omega_2$,	63·3	(−39·5)	69·5	+6·2
		Mean .. .. $\omega+\omega_2$ =		181·2				Mean .. $\omega'+\omega_2'$ =		−46·0		

TABLE V.—Acids, &c.

			$\omega_1+\omega_2$ calculated.					$\omega_1'+\omega_2'$ calculated.			
Acids—											
Formic acid . ..	$H.CO_2H$	$\alpha-\omega_1-\omega_2$; $\frac{1}{2}\alpha-\omega_1$	69·1	141·7	69·0	−0·1	−0·14	$\alpha'-\omega_1'-\omega_2'$	95·4	−74·2	95·5	+0·1
Acetic acid . ..	$CH_3.CO_2H$	$2\alpha-\beta-\omega_1-\omega_2$; $1\frac{1}{2}\alpha-\beta-\omega_1$	224·8	144·3	227·3	+2·5	+1·11	$2\alpha'-\beta'-\omega_1'-\omega_2'$	104·1	−76·7	101·7	−2·4
Propionic acid ..	$C_2H_5.CO_2H$	$3\alpha-2\beta-\omega_1-\omega_2$; $2\frac{1}{2}\alpha-2\beta-\omega_1$	385·6	141·8	385·6	0·0	0·00	$3\alpha'-2\beta'-\omega_1'-\omega_2'$	107·7	−74·1	107·9	+0·2
		Mean.. .. $\omega_1+\omega_2$ =		142·4				Mean .. $\omega_1'+\omega_2'$ =		−75·0		
Acetic anhydride .	$(CH_3CO)_2O$	$4\alpha-2\beta-\omega-2\omega_2$; $3\alpha-2\beta-\omega$	459·5	—	452·0	−7·5	−1·63	$4\alpha'-2\beta'-\omega'-2\omega_2'$	130·8	—	138·4	+7·6

TABLE VI.—*The Fundamental Molecular Heat of Combustion and Formation, Oxygen Constants.*

Class of oxygen linkage.	Class of substance.	M.H.C. (cals.).	M.H.F. (cals.).
Etheric oxygen	Ethers, $R.O.R_1$; Esters, $R.C\overset{O}{\lessdot}_{OR_1}$	$\omega = 75{\cdot}4$	$\omega' = -7{\cdot}8$
Hydroxylic oxygen	Alcohols (Group 1, see text)	$\omega_1 = 29{\cdot}7$	$\omega_1' = -\omega_1 = -29{\cdot}7$
	Alcohols (Group 2, see text) ; Acids, $R.C\overset{O}{\lessdot}_{OH}$	$\omega_1 = 36{\cdot}4$	$\omega_1' = -\omega_1 = -36{\cdot}4$
Ketonic oxygen	Aldehydes, $R.C\overset{O}{\lessdot}_{H}$ (?)	$\omega_2 = 87{\cdot}7$	$\omega_2 = -20{\cdot}2$
	Ketones, $R.C\overset{O}{\lessdot}_{R_1}$ (?)	$\omega_2 = 91{\cdot}4$	$\omega_2' = -23{\cdot}7$
	Carbon dioxide ; Esters, $R.C\overset{O}{\lessdot}_{OR_1}$; Acids, $R.C\overset{O}{\lessdot}_{OH}$	$\omega_2 = \frac{\alpha}{2} = 105{\cdot}4$	$\omega_2' = -37{\cdot}9$

The value of $\omega+\omega_2$ obtained from each acid is given in the table. The mean value (neglecting the values obtained from ethyl acetate and allyl formate, which diverge rather greatly from the mean) = 181·2 cals. It is at once evident that if we assign to ω_2 the values obtained from either aldehydes or ketones, values for ω will be obtained which are much higher than obtained before (CHEMICAL NEWS, xcvii., p. 253); but if, on the other hand, we assign to ω_2 the value 105·4 cals. obtained from a consideration of carbon dioxide, a value for ω, namely, 75·8 cals., is obtained in excellent agreement with that obtained from ethers, namely, 75·4 cals.

It is evident, therefore, that as the value of ω_2 in these esters is equivalent to $\frac{\alpha}{2}$, their formulæ, in so far as molecular heats of *combustion* are concerned, can be simplified, the general formula becoming :—

$$(n-\tfrac{1}{2})\alpha-(n+p-a-b-1)\beta-a\gamma-b\delta-\omega.$$

Both sets of formulæ are given in Table IV.; using the simplified one and the value $\omega = 75{\cdot}4$ cals., the molecular heats of combustion of all the esters given have been calculated, and are exhibited together with the differences between them and the experimental, and the percentage errors in Table IV. The agreement is quite satisfactory, except in the case of ethyl acetate, which gives an exceptional molecular heat of combustion, which has not yet been satisfactorily explained (see Thomsen, "Thermochemische Untersuchungen," iv., p. 310).

8. *Molecular Heats of Combustion of Acids.*

The general formula for all monobasic carboxy acids is—

$$nC+2(n-a-2b-p-\tfrac{1}{2})H+(n+p-a-b-1)L_1+$$
$$+aL_2+bL_3+2O+1(C:O)\text{ link }+$$
$$+1(C.O)\text{ link }+1(O.H)\text{ link }+H\text{ (linked to O, not C).}$$
$$=nC2(n+1-a-2b-p)H+$$
$$+(n+p-a-b-1)L_1+aL_2+bL_3-\omega_1-\omega_2.$$
$$=n\alpha-(n+p-a-b-1)\beta-a\gamma-b\delta-\omega_1-\omega_2.$$

In Table V. will be found the molecular heats of combustion (corrected for constant volume) of three acids given by Thomsen; from these the value of $\omega_1+\omega_2$ has been calculated thus :—

Formic acid is $H.C\overset{O}{\lessdot}_{OH}$; *i.e.*, $\alpha-\omega_1-\omega_2$. M.H.C. found = 69·1 cals. Therefore $\omega_1+\omega_2 = \alpha-69{\cdot}1$ cals. = (210·8 − 69·1) cals. = 141·7 cals. The value of $\omega_1+\omega_2$ obtained from each acid is given in the table. Mean value $\omega_1+\omega_2 = 142{\cdot}4$ cals. It is at once evident that if we assign to ω_2 the values obtained from either aldehydes or ketones, values for ω_1 will be obtained which are much higher than obtained before (CHEMICAL NEWS, xcvii., p. 255); but if, on the other hand, we assign to ω_2 the value 105·4 cals. obtained from the consideration of carbon dioxide, we obtain for ω_1 a value 37·0 cals. in agreement with that found for the second group of alcohols, namely, 35·9 cals. The mean of these two values, namely, 36·4 cals., is therefore taken as the value of ω_1 for these classes of compounds.

It is evident therefore that as the value of ω_2 in these acids is equivalent to $\frac{\alpha}{2}$ their formulæ, in so far as molecular heats of *combustion* are concerned, can be simplified as were the formulæ of their esters with monohydroxy alcohols, the general formula becoming :—

$$(n-\tfrac{1}{2})\alpha-(n+p-a-b-1)\beta-a\gamma-b\delta-\omega_1.$$

Both sets of formulæ are given in Table V.; using the simplified fromulæ and the value $\omega_1 = 36{\cdot}4$ cals. the molecular heats of combustion of the acids (and also similarly that of acetic anhydride, using $\omega = 75{\cdot}4$ cals.) have been calculated, and are exhibited together with the differences between them and the experimental and the percentage errors in Table V. The agreement in the cases of the acids is quite satisfactory.

9. *Molecular Heats of Formation of Esters and Acids.*

The values of $\omega'+\omega_2'$ and $\omega_1'+\omega_2'$ have been similarly calculated from the molecular heats of formation of the esters and acids respectively, as were the corresponding molecular heat of combustion constants. The mean values are $\omega'+\omega_2' = -46{\cdot}0$ cals. and $\omega_1'+\omega_2' = -75{\cdot}0$ cals. in agreement with the values of ω', ω_1', and ω_2', as obtained respectively from ethers, alcohols (second group), and carbon dioxide. Using these values, namely, $\omega'+\omega_2' = -45{\cdot}7$ cals., $\omega_1'+\omega_2' = -74{\cdot}3$ cals., the molecular heats of formation of all these esters, acids, &c., given, have been calculated, and are exhibited together with the differences between them and the experimental in Tables IV. and V.

10. *Summary and Conclusion.*

In the two foregoing papers the molecular heats of combustion (and formation) of all the organic oxygen compounds given by Thomsen (excluding necessarily those containing elements whose thermal behaviours have not yet been considered; and also the following: carbon monoxide, whose formula is doubtful; carbonylchloride, trimethylorthoformate, and dimethyl and diethyl carbonates, which give anomalous results) have been considered, and by means of the author's system of "fundamental constants" (the values of which are exhibited in Table VI.) perfectly satisfactory results have been obtained for the molecular heats of combustion (and formation) of thirty-four substances out of the thirty-eight considered.

At a later date it is hoped that with the accumulation of data, explanations may be offered of the anomalous substances.

The Polytechnic, Regent Street, W.

THE ETHER OF SPACE.*

By Sir OLIVER LODGE, LL.D., D.Sc., F.R.S.

(Concluded from p. 258).

Appendix I.—On Gravity and Etherial Tension.

Stating the law of gravitation as $F = \gamma \frac{m\,m'}{r^2}$, the meaning here adopted for etherial tension at the surface of the earth is—

$$T = \int_R^\infty \frac{\gamma E}{r^2} dr = \frac{\gamma E}{R} ;$$

so that the ordinary intensity of gravity is—

$$g = -\frac{dT}{dR} = \frac{\gamma E}{R^2} = \frac{4}{3}\pi\rho\gamma R.$$

Accordingly, near the surface of a planet the tension is $T_0 = g\,R$, or for different planets in proportional to $\rho\,R_2$.

The velocity of free fall from infinity to such a planet is $\sqrt{(2\,T_0)}$; the velocity of free fall from circumference to centre, assuming uniform distribution of density, is $\sqrt{(T^0)}$; and from infinity to centre it is $\sqrt{(3\,T_0)}$.

Expanding all this into words :—

The etherial tension near the earth's surface, required to explain gravity by its rate of variation, is of the order 6×10^{11} c.g.s. units. The tension near the sun is 2500 times as great. With different spheres in general, it is proportional to the density and to the superficial area. Hence, near a bullet one inch in diameter, it is of the order 10^{-6}; and near an atom or electron about 10^{-21}.

In order to set up a tension equal to the critical, or presumably disruptive, stress in the ether [10^{33} c.g.s.], a globe of the density of the earth would have to have a radius of eight light years. In order to generate a velocity of free fall under gravity equal to the velocity of light, a globe of the earth's density would have to be equal in radius to the distance of the earth from the sun, or say 26,000 times the earth's radius. If the density were less, the superficial area would have to be increased in proportion, so as to keep $\rho\,R^2$ constant.

The whole visible universe within a parallax of 1/1000 second of arc, estimated by Lord Kelvin as the equivalent of 10^9 suns, would be quite incompetent to raise etherial tension to the critical point 10^{33} c.g.s., unless it were concentrated to an absurd degree; but it could generate the velocity of light with a density comparable to that of water.

If the average density of the above visible universe (which may be taken as $1{\cdot}6 \times 10^{-23}$ grms. per cc.) continued without limit, a disruptive tension of the ether would be reached when the radius was comparable to 10^{13} light years; and the velocity of light would be generated by it when the radius was 10^7 light years. But heterogeneity would enable these values to be reached *more* easily.

It is noteworthy how exceedingly small is the average or aggregate density of matter in the visible region of space; and Lord Kelvin has shown that throughout space in general it must be smaller still—in fact ultimately infinitesimal.

The estimated density of 10^{-23} c.g.s. means that the visible cosmos is as much rarer than a vacuum of a hundred millionths of an atmosphere, as that vacuum is itself rarer than lead.

It is, of course, because ordinary masses of matter likewise consist of separated particles, with great intervening distances in proportion to their size, that we are able to assert the minute aggregate density of ordinary stuff, such as water or lead, as compared with the continuous medium of which all particles are supposed to be really composed. The fundamental medium itself must be of uniform density everywhere, whether materialised or free.

* Abstract of a Discourse delivered at the Royal Institution, February 21, 1908.

Appendix II.—Explanatory Remarks concerning the Density of Ether.

I observe that it is surmised by at least one thoughtful and friendly critic—C. W. S. in the *Westminster Gazette*—that in speaking of the immense density or massiveness of ether, and the absurdly small density or specific gravity of gross matter by comparison, I intended to signify that matter is a *rarefaction* of the ether. That, however, was not my intention. The view I advocate is that the ether is a perfect *continuum*, an absolute *plenum*, and that therefore no rarefaction is possible. The ether inside matter is just as dense as the ether outside, and no denser. A material unit—say an electron—is only a peculiarity or singularity of some kind in the ether itself, which is of perfectly uniform density everywhere. What we sense as matter is an aggregate or grouping of an enormous number of such units.

How then can we say that matter is millions of times rarer or less substantial than the ether of which it is essentially composed? Those who feel any difficulty here should bethink themselves of what they mean by the average or aggregate density of any discontinuous system, such as a powder, or a gas, or a precipitate, or a snowstorm, or a cloud, or a milky way.

If it be urged that it is unfair to compare an obviously discrete assemblage like the stars, with an apparently continuous substance like air or lead, the answer is that it is entirely and accurately fair; since air, and every other known form of matter, is essentially an aggregate of particles, and since it is always their average density that we mean. We do not even know for certain their individual atomic density.

The phrase "specific gravity or density of a powder" is ambiguous. It may mean the specific gravity of the dry powder as it lies, like snow; or it may mean the specific gravity of the particles of which it is composed, like ice.

So also with regard to the density of matter, we might mean the density of the fundamental material of which its units are made—which would be ether; or we might, and in practice do, mean the density of the aggregate lump which we can see and handle; that is to say, of water or iron or lead, as the case may be.

In saying that the density of matter is small, I mean, of course, in the last, the usual, sense. In saying that the density of ether is great, I mean that the actual stuff of which these highly porous aggregates are composed is of immense, of well-nigh incredible, density. It is only another way of saying that the ultimate units of matter are few and far between—*i.e.*, that they are excessively small as compared with the distances between them; just as the planets of the solar system, or worlds in the sky, are few and far between—the intervening distances being enormous as compared with the portions of space actually occupied by lumps of matter.

Here it may be noted that it is possible to argue that the density of a *continuum* is necessarily greater than the density of any disconnected aggregate: certainly of any assemblage whose particles are actually composed of the material of the *continuum*. Because the former is "all there," everywhere, without break or intermittence of any kind; while the latter has gaps in it—it is here, and there, but not everywhere.

Indeed, this very argument was used long ago by that notable genius Robert Hooke, and I quote a passage which Professor Poynting has discovered in his collected posthumous works, and kindly copied out for me :—

"As for *matter*, that I conceive in its essence to be immutable, and its essence being expatiation determinate, it cannot be altered in its quantity, either by condensation or rarefaction; that is, there cannot be more or less of that power or reality, whatever it be, within the same expatiation or content; but every equal expatiation contains, is filled, or is an equal quantity of *materia*; and the densest or heaviest, or most powerful body in the world contains no more materia than that which we conceive to be the rarest, thinnest, lightest, or least powerful body of

all; as gold, for instance, and *æther*, or the substance that fills the cavity of an exhausted vessel, or cavity of the glass of a barometer above the quicksilver. Nay, as I shall afterwards prove, this cavity is more full, or a more dense body of æther, in the common sense or acceptation of the word, than gold is of gold, bulk for bulk; and that because the one, viz., the mass of æther, is all æther: but the mass of gold, which we conceive, is not all gold; but there is an intermixture, and that vastly more than is commonly supposed, of æther with it; so that vacuity, as it is commonly thought, or erroneously supposed, is a more dense body than the gold as gold. But if we consider the whole content of the one with that of the other, within the same or equal quantity of expatiation, then are they both equally containing the *materia* or body."—From the "Posthumous Works of Robert Hooke, M.D., F.R.S.," 1705, p. 171 (as copied in "Memoir of Dalton," by Angus Smith).

Newton's contemporaries did not excel in power of clear expression, as he himself did, but Professor Poynting interprets this singular attempt at utterance thus:—"All space is filled with equally dense *materia*. Gold fills only a small fraction of the space assigned to it, and yet has a big mass. How much greater must be the total mass filling that space."

The tacit assumption here made is that the particles of the aggregate are all composed of one and the same continuous substance, practically that matter is made of ether; and that assumption, in Hooke's day, must have been only a speculation. But it is the kind of speculation which time is justifying, it is the kind of truth which we all feel to be in process of establishment now.

We do not depend on that sort of argument, however; what we depend on is experimental measure of the mass, and mathematical estimate of the volume, of the electron. For calculation shows that however the mass be accounted for, whether electrostatically or magnetically, or hydrodynamically, the estimate of ratio of mass to effective volume can differ only in a numerical coefficient, and cannot differ as regards order of magnitude. The only way out of this conclusion would be the discovery that the negative electron is not the real or the main matter-unit, but is only a subsidiary ingredient, whereas the main mass is the more bulky positive charge. That last hypothesis, however, is at present too vague to be useful. Moreover, the mass of such a charge would in that case be unexplained, and would need a further step, which would probably land us in much the same sort of etherial density as is involved in the estimate which I have based on the more familiar and tractable negative electron.

It may be said why assume any finite density for the ether at all? Why not assume that, as it is infinitely continuous, so it is infinitely dense—whatever that may mean—and that all its properties are infinite? This might be possible were it not for the velocity of light. By transmitting waves at a finite and measurable speed, the ether has given itself away, and has let in all the possibilities of calculation and numerical statement. Its properties are thereby exhibited as essentially finite—however infinite the whole extent of it may turn out to be.

ON THE PURIFICATION OF PEATY WATERS BY FREEZING.

By FRANK T. SHUTT, M.A., F.I.C.,
Chemist, Dominion Experimental Farms.

In the course of an investigation to ascertain the relative purity of the ice from the Ottawa and Rideau Rivers, certain data were obtained of an interesting character, illustrative of the purification of "upland, surface" waters by freezing.

Both waters are "peaty" and highly coloured, and they are, further, characterised by a very small mineral content. The Ottawa river, by reason of its much larger body of water, its succession of rapids and water-falls, and its passage through a country less likely to contaminate it, naturally offers a more favourable source for supply than the Rideau river, which, in addition to its smaller volume and much shorter length, is at intervals through a considerable portion of its course rendered more or less stagnant by the locks which serve to convert the river into a canal system.

Analyses of these river waters made in the month of November are presented; they serve to show that the differences in the nature or quality of the waters is one of degree rather than of kind. Presumably, both rivers, at the point of collection, are unpolluted.

Analysis of Waters of Ottawa and Rideau Rivers (parts per million).

	Ottawa River (above Chaudiere Falls).	Rideau River (above Billings Bridge).
Free ammonia	0·012	0·024
Albumenoid ammonia	0·227	0·40
Nitrogen as nitrates and nitrites	0·113	0·034
Chlorine	0·6	2·5
Total solids at 212° F.	56·0	145·2
Solids after ignition .	24·8	82·8

That both waters contain large quantities of dissolved vegetable organic matter is evident from the high figures for the albumenoid ammonia; the Ottawa river water, however, it will be remarked, is in this respect much the purer. There would be no object for the purposes of this paper in critically considering and comparing these data, but it may be pointed out in passing, that they show the superior quality of the Ottawa river water in many respects—a conclusion that is in accord with our prediction from a knowledge of the rivers and the country through which they travel.

Ice from Ottawa and Rideau Rivers.

The ice blocks analysed were cut in February, when the thickness of the ice on the Ottawa river was about 22 inches; that on the Rideau river, about 18 inches. Both blocks showed from 4 to 6 inches on the surface of so-called "snow" or "slush" ice: *i.e.*, ice formed partly of snow. This layer of ice, which, though not so transparent as the rest of the block, was nevertheless fairly solid and clean. From inspection one would say that both ices were satisfactory, being clear, non-porous, and practically free from suspended matter.

Thoroughly representative samples were procured by sawing a section, about 5 inches wide, from the centre of each block and throughout its whole thickness. The ice thus obtained was broken up and allowed to melt in a clean covered vessel, the resulting waters constituting the first series as follows:—

Analysis of Ice (parts per million).

	From Ottawa River (above Chaudiere Falls).	From Rideau River (above Billings Bridge).
Free ammonia	0·04	0·06
Albumenoid ammonia	0·041	0·135
Nitrogen as nitrates and nitrites	0·049	0·049
Chlorine	0·05	0·15
Total solids at 212° F.	4·4	5·4
Solids after ignition .	Trace	Trace

Comparing these data with those of the waters previously given, it is at once apparent that, in freezing, a very large quantity of dissolved organic matter has been eliminated. Taking, first, the albumenoid ammonia as an index of this peaty matter, it will be noticed that the reduction by freezing in the case of the Ottawa river is from 0·227 p.p.m. to 0·041 p.p.m., and in that of the Rideau river from 0·400 p.p.m. to 0·135 p.p.m. Similarly with the "Total Solids," practically half of which is organic matter, the reduction from freezing has been from

56 p.p.m., and 145·2 p.p.m. to 4·4 p.p.m. and 5·4 p.p.m. respectively. The chlorine is also much reduced, and the mineral matter (solids after ignition) entirely disappears.

Purification by freezing has long been known, but the data on record in this regard refer more particularly to the exclusion of mineral matter. The extent to which dissolved vegetable matter may be thrown out by freezing, as made evident by these results, has seemed to the writer somewhat remarkable and worthy of note.

To obtain some further knowledge respecting this exclusion of peaty matter by freezing, 1000 cc. of the Ottawa river water were placed in a porcelain basin and submitted to the action of frost until the greater portion of the water was converted into ice. Upon removal of the ice it was found that 125 cc. of the original water still remained unfrozen, the ice representing 875 cc. Analyses of each were made, and the results show that under such conditions a very considerable elimination of the organic matter had taken place during the freezing process.

	Ice (p.p.m).	Water (p.p.m.).
Free ammonia	0·01	0·08
Albumenoid ammonia	0·175	0·40

A calculation from these results of the amounts of free and albumenoid ammonia in the original water furnishes data in close accord with those obtained by direct analysis.

The degree of purification is dependent on several factors. According to recognised authorities, ice forming on deep water is purer than that on shallow water—the quality of both waters being initially the same. The slower the ice formation, the purer the ice. The thicker the ice, within certain limits, the purer it is; and, lastly, it is held that the lower part of the ice block will be of better quality than that nearer the surface.

Purification by freezing is, after all, however, but partial. Undoubtedly under the most favourable conditions a very large proportion of the mineral and organic constituents may be thrown out, and the bacterial content considerably reduced; but it has been clearly shown that the elimination is never such that the ice cut from a polluted source is safe for domestic purposes.

The investigation has been continued to ascertain the purity of the ice in relation to its position in the block, but the data as yet are incomplete and are, therefore, reserved for presentation at some future time.—*Transactions of the Royal Society of Canada*, i., p. 31.

THE DETERMINATION OF ANTIMONY AND ARSENIC IN LEAD-ANTIMONY ALLOYS.

By GEORGE M. HOWARD.

The separation and determination of antimony and arsenic in alloys with anything like commercial rapidity, and at the same time with a fair degree of accuracy, is by no means a simple matter. The apparent lack of satisfactory published methods led to the development several years ago of the method here described, which, while involving nothing radically new, has proved very serviceable in the author's laboratory.

One great advantage of this method is that tin does not interfere, and does not have to be removed, which makes it available for type metal, &c. Iron and copper in small amounts are also without effect, and in fact there seems to be nothing at all likely to be present which interferes. The method is applicable also to many other cases besides lead-antimony alloys—as, for instance, to the mixed sulphides of antimony and arsenic obtained in many analyses. Some operators object seriously to any method involving the use of hydrogen sulphide, but if the details of manipulation here given are followed there will be no inconvenience whatever from that source.

The procedure is as follows:—

The sample in fine filings, 0·5 to 2 grms. according to circumstances, is weighed into a 125 cc. Erlenmeyer flask, 60 to 70 cc. of strong hydrochloric acid added, and two or three drops (not more) of nitric acid (1·4). The flask is then placed on a hot plate where it will be just short of boiling until solution is complete. Frequent agitation considerably hastens the action. It is sometimes necessary to make further additions of nitric acid, but this should be done carefully, and an excess avoided. When the metal is all dissolved (ten to twenty minutes) the flask should be removed where it will boil vigorously for a few minutes until the colour changes from reddish yellow to colourless—or, if iron or copper is present, to straw-yellow. Now, while still hot, hydrogen sulphide is passed into the solution until it is completely saturated—fifteen minutes is usually sufficient. If insufficient hydrochloric acid has been used, or the solution has been boiled so long on the plate that much has been lost, antimony sulphide will be precipitated as the solution cools. The hydrogen sulphide treatment is most conveniently handled by fitting the flasks with two-hole stoppers and inlet and outlet tubes, and connecting several in series to the generator. If the outlet from the last flask is led into a bottle of caustic soda solution, no gas whatever comes off free. When saturated, the flasks are transferred to a current of air, still in series, and again absorbing the gas from the last flask in caustic soda, and the air passed until all the hydrogen sulphide is removed (half an-hour is sufficient for two flasks). The hydrogen sulphide precipitates nothing but arsenic as sulphide, but reduces all salts capable of reduction—antimony, tin, copper, iron, &c. The current of air then re-oxidises all of these except the antimony, which remains in the antimonious form.

To the now cold solution a little tartaric acid is added, and water until its bulk is about doubled, when it is filtered, best through a double filter, into a 16 oz. flask. Practically all of the lead chloride must be washed out of the precipitate with hot water, but it is not necessary to add all the washings to the filtrate, as the antimonious chloride is readily washed out by decantation with cold water.

Antimony.—The filtrate is nearly neutralised by adding powdered sodium carbonate in small portions, care being used not to reach the point of precipitation of the lead, or, if this is reached, making it slightly acid again with hydrochloric acid. The neutralisation is then completed with sodium bicarbonate, and a slight excess added (about one spoonful of powder). The antimony is then determined by titrating with standard iodine solution, using fresh starch solution as indicator. The precipitate of lead carbonate does not affect the titration, and with a little practice the end-point can be recognised just as easily as in a clear solution. Too much starch should be avoided, as it makes the end-point obscure. A convenient strength for the iodine solution is 1 cc. = 0·005 grm. antimony, then with 0·5 grm. samples 1 cc. = 1 per cent antimony.

If arsenic is negligibly low—which, with a little experience, can be pretty well gauged by the appearance of the precipitate—or for any reason is not to be determined, the filtering may be dispensed with. In this case the whole solution, with the arsenious sulphide, if any, and free sulphur in suspension, is merely transferred to a larger flask, neutralised and titrated. The suspended arsenious sulphide and free sulphur are without effect.

Arsenic.—The bulk of the arsenious sulphide and sulphur is washed off the filter back into the same flask in which the precipitation was made, using not over 20 cc. or so of water. A few drops of sodium hydroxide are added (five drops of 20 per cent solution is ample), the solution boiled for a few moments, and then decanted through the filter into an 8 oz. Erlenmeyer flask. This weak soda readily dissolves the arsenious sulphide, while taking up only a small part of the free sulphur. If the amount of precipitate is at all considerable, it is safer to give a second treatment with soda solution.

The filter is washed with hot water, and discarded. To the filtrate is added hydrogen peroxide solution, which

should be reasonably fresh, or else its strength known. Twenty cc. of 3 per cent solution is sufficient for arsenic up to several per cent. The hydrogen peroxide oxidises the arsenic, and also all sulphur compounds, giving a colourless solution. This is now boiled down to a small bulk, about 20 cc., the excess of peroxide being decomposed in the process. When cool, potassium iodide solution is added in amount equivalent to about 0·1 grm. KI, then 20 cc. of strong hydrochloric acid. After standing five minutes it is cooled and titrated with standard thiosulphate, adding three drops of starch solution only when the colour is almost gone. A convenient strength for the thiosulphate solution is 1 cc. = 0·001 grm. arsenic, and it should, of course, be frequently standardised. It is well, also, to run a blank titration, using the same amounts of reagents as in the analysis, to determine whether there is any constant to be deducted from the burette reading, due to impurities in the reagents.

The difficulty with the end-point experienced by many in this titration appears to be due to using too large an excess of potassium iodide and too much starch. With the proportions given above, the end-point is exceedingly sharp, and the reaction seems to be just as complete as when more potassium iodide is used. The heating due to adding the strong hydrochloric acid is sufficient without any digesting, as is sometimes recommended.

After oxidising and concentrating, the arsenic is in a form to be readily determined in several ways, although the above method is preferred on account of ease and rapidity. For instance, the arsenic may be precipitated with silver nitrate as silver arsenate, after neutralisation with acetic acid, and the combined silver titrated with thiocyanate, as in the well known modified Pearce method. In this case care must be used to wash the sulphide free from lead chloride, and also to have all reagents free from chlorine (most of the hydrogen peroxide solutions on the market contain hydrochloric acid). Or the arsenic may be determined gravimetrically by precipitation as ammonium magnesium arsenate. In this case it is better to use ammonia instead of sodium hydroxide to dissolve the arsenious sulphide.—*Journal of the American Chemical Society*, xxx., No. 3.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 21st, 1908.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

MESSRS. G. Barr, C. Gilling, G. R. Lynch, W. E. Oakden, D. R. Pinnock, and W. H. Withey were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William Henry Ballantyne, B.Sc., 99, Holmdene Avenue, Herne Hill, S.E.; Edward Morris Bevan, 10, Coronation Street, Aberkenfig, Glam.; James Brown, 20, Tower Road, Dartford, Kent; James Hill Fairweather, 62, Wythes Road, Silvertown, E.; Frank William Crossley-Holland, Connaught Club, Marble Arch, W.; Alfred Ash Meggitt, B.Sc., Dacca, Eastern Bengal, India; Clement Thomas Rutter, 4, Bath Terrace, Hanwell, W.; James Edward Southcombe, M.Sc., 138, Chester Street, Birkenhead, Cheshire; Edward Stokes, B.A., King William's College, Isle of Man; Harry James Yates, Redcroft, Four Oaks, Warwickshire.

A certificate has been authorised by the Council under By-law I. (Par. 3) in favour of Hari Prasad Vidyant, Etawah, U.P., India.

Of the following papers, those marked * were read:—

*110. "*Hydroaromatic Ketones.*" (Preliminary Note). By ARTHUR WILLIAM CROSSLEY and CHARLES GILLING.

5-Chloro-1 : 1-dimethyl-Δ^4-*cyclo*hexenone-3 (I.) reacts readily with ethyl malonate in presence of sodium ethoxide to give *ethyl* 1 : 1-*dimethyl*-Δ^4-cyclo*hexen*-3-*one*-5-*acetate* (II.). During the condensation, one of the carbethoxy-groups of the ethyl malonate is evidently hydrolysed by the sodium ethoxide, and the resulting carboxyl group loses the elements of carbon dioxide (compare Moore, *Trans.*, 1904, lxxxv., 165).

$$CMe_2\!<\!\begin{matrix}CH_2\text{—}CO\\ CH_2\cdot CCl\!=\!CH\end{matrix}\!> \rightarrow$$

I.

$$\rightarrow CMe_2\!<\!\begin{matrix}CH_2\text{———}CO\\ CH_2\cdot C(CH_2\cdot CO_2Et)\!=\!CH\end{matrix}\!>.$$

II.

The ester is a faintly yellow oil, boiling at 171°/22 mm., and possessing a slight ethereal odour. It gives a *semicarbazone* melting at 156—157° without decomposition. When hydrolysed with alcoholic potassium hydroxide, the corresponding acid cannot be isolated, as it at once loses carbon dioxide to give 1 : 1 : 5-*trimethyl*-Δ^4-cyclo*hexenone*-3 (III.) as a colourless, highly refractive liquid, boiling at 108°/35 mm., and possessing a slight camphoraceous odour. The *semicarbazone* crystallises from alcohol in clusters of flattened needles melting at 190—191°, and the *oxime* forms large transparent prisms melting at 78°. When oxidised with potassium permanganate, a variety of products are obtained, according to the conditions employed. One acid, melting at 98°, has been proved to have the composition $C_9H_{14}O_4$, and its constitution is most probably represented by Formula IV.

$$CMe_2\!<\!\begin{matrix}CH_2\text{—}CO\\ CH_2\cdot CMe\end{matrix}\!\!>\!CH.$$

III.

$$CMe_2\!<\!\begin{matrix}CH_2\text{——}CO\\ CH_2\cdot C(CH_3)\end{matrix}\!\!>\!CH \rightarrow CMe_2\!<\!\begin{matrix}CH_2\cdot CO\cdot CO_2H\\ CH_2\cdot CO\cdot CH_3\end{matrix}.$$

IV.

The reaction appears to be a general one, for 5-chloro-1 : 1-dimethyl-Δ^4-*cyclo*hexenone-3 condenses with ethyl ethylmalonate in presence of sodium ethoxide, and the product on hydrolysis yields 1 : 1-*dimethyl*-5-*propyl*-Δ^4-cyclo*hexenone*-3, $CMe_2\!<\!\begin{matrix}CH_2\text{——}CO\\ CH_2\cdot C(C_3H_7)\end{matrix}\!\!>\!CH$, boiling at 125°/19 mm., and possessing an odour of celery and camphor. The *semicarbazone* crystallises from alcohol in rosettes of flattened needles melting at 156°. The work is being extended, and the products and by-products of the various reactions are under closer investigation.

*111. "*The Sulphides and Oxysulphides of Silicon.*" By IRVINE GILES RANKIN and SIDNEY MONTAGU REVINGTON.

The white sulphide of silicon, first prepared by Berzelius, has been shown definitely to be the disulphide, SiS_2. The orange sulphide, SiS, prepared by Colson, has been investigated, and, in addition, the composition of two sulphoxides, SiSO and $SiSO_2$, has been determined; the former is mentioned by Colson, but was not analysed by him, whilst the latter has been hitherto unknown.

DISCUSSION.

The PRESIDENT congratulated Mr. Revington and Mr. Rankin on the results they had obtained. He could testify to their perseverance, and, although the analyses which they had quoted were not so concordant as is usual, the difficulties of separating and obtaining in a pure state three such bodies as SiS_2, SiOS, and SiS were great, and at present, at all events, we had to be content with what were great improvements on former results.

*112. "*Apparatus for Experiments at High Temperatures and Pressures, and its Application to the Study of Carbon.*" By Richard Threlfall.

The author described a small and inexpensive laboratory apparatus for exposing carbon or other substances to very high temperatures and pressures. It was shown how small quantities of material may be heated up to the temperature of the melting-point of magnesia at pressures up to 100 tons per square inch. These results are rendered possible by taking advantage of the practically perfect fluidity of crystalline graphite under high pressures. Instead of using compressed gases, as has hitherto been done in order to obtain high pressures, it is only necessary to make use of crystalline graphite, which is, of course, very much more easily and safely handled. The graphite itself acts as a conductor whereby electric heating is rendered possible.

Some experiments on heating graphite or amorphous carbon up to the melting-point of magnesia at pressures up to 100 tons per square inch were described. In no case was anything produced but soft crystalline graphite, the results obtained agreeing precisely with those already published by Parsons (*Proc. Roy. Soc.*, 1907, lxxix., A, 532).

A summary was given of our present information in regard to the transformation of carbon, and the view is taken that the formation of diamond under certain conditions is not so much a direct transformation of carbon as the result of the liberation of carbon by decomposition of carbides in presence of certain substances which induce it to crystallise in any of the well known forms of diamond. These substances can be recognised by a study of the ash left when diamonds are burnt. The only condition as to temperature is that it must be low enough for the velocity of transformation into graphite to be small. The results obtained by Hasslinger and others were examined from this point of view.

*113. "*Acids as Accelerators in the Acetylation of Amino-groups.*" By Alice Emily Smith and Kennedy Joseph Previté Orton.

When the basic properties of amino-groups are in abeyance, acids act as powerful accelerators of acetylation by means of acetic anhydride. Such amino-groups are present in anilines with two negative groups in the ortho-positions with respect to the amino-group.

All strong acids, very small quantities of which are alone needed, act in this manner. Sulphuric, hydrochloric, perchloric, trichloroacetic, nitric, and chromic acids have been tested; the two latter behave exceptionally, yielding respectively nitroaminobenzene, $Ar{\cdot}NH{\cdot}NO_2$, and products of oxidation of the aniline.

The formation of diacetyl as well as of monoacetyl derivatives of the anilines is aided by the presence of acids.

In the case of basic amino-groups, the reaction of which with acetic anhydride, even when largely diluted by a neutral solvent, is extremely rapid, acids act as mild inhibitors of acetylation.

Details of the preparation of typical mono- and di-acetanilides with the aid of strong acids were described.

*114. "*The Chemical Action of Radium Emanation.* Part III. *On Water and certain Gases.*" By Alexander Thomas Cameron and Sir William Ramsay, K.C.B.

The decomposition of water and the re-combination of hydrogen and oxygen, when treated with radium emanation, have been confirmed by numerous experiments. Carbon dioxide is decomposed into carbon, oxygen, and the monoxide. The last named gives carbon, oxygen, and the dioxide. Ammonia breaks up into its components. These re-combine, but in smaller quantity, for the same amount of emanation. Hydrogen chloride is decomposed into hydrogen and chlorine. At 130°, hydrogen and oxygen re-combine during five hours at a steady rate; steam is apparently undecomposed. The time rates of the various reactions were measured; the volume was kept constant, and change of pressure indicated the rate of change. This was in all cases proportional to the rate of change of the emanation. In other words, it obeyed the same exponential law; the amount of change in any time was strictly proportional to the amount of emanation disintegrating in that time. Hence, other conditions being the same, each atom of emanation, as it disintegrates, produces a certain definite chemical effect.

*115. "*The Chemical Action of Radium Emanation.* Part IV. *On Water.*" By Alexander Thomas Cameron and Sir William Ramsay, K.C.B.

The results obtained in a previous experiment (*Trans.*, 1907, xci., 1593) have been confirmed; radium emanation in presence of water breaks up into neon. The neon was conclusively identified by its spectrum; the lines were almost as bright as those of the helium visible at the same time. The spectrum was photographed successfully, and a large number of the neon lines identified. It faded rapidly; the neon lines practically disappeared in ten minutes.

116. "*Titani-dihydroxymaleic Acid and the Detection of Titanium.*" By Henry John Horstman Fenton.

Dihydroxymaleic acid reacts in cold dilute aqueous solution with quadrivalent titanium compounds, giving an intensely reddish brown solution. The reaction is so sensitive that it serves for the detection of minute traces of titanium. It is very much more delicate than the hydrogen dioxide test, and has the additional advantage that it is not given by vanadium.

From more concentrated solutions, a voluminous chocolate-coloured precipitate separates which has the empirical composition $C_4H_4O_6,2TiO_2,2\frac{1}{2}H_2O$. This compound acts as an acid, giving, when treated with alkalis, bright orange-coloured salts.

Compounds having a similar composition have previously been obtained with many other aliphatic acids, but they are all colourless.

The coloured compound obtained with dihydroxymaleic acid is at once destroyed by hydrofluoric acid or soluble fluorides, and may, as in the case of the hydrogen dioxide reaction, be employed for the detection of fluorides. Owing to the marked difference in colour between the acid and its salts, the compound may also be used as an alkali-acid indicator.

117. "*The Preparation of Diselenides. Dibenzyl Diselenide.*" (Preliminary Note). By Thomas Slater Price and Lionel Manfred Jones.

The method employed by Price and Twiss (*Trans.*, 1907, xci., 2021) for the preparation of disulphides has been extended to the preparation of diselenides. A solution of sodium selenosulphate was obtained by digesting excess of selenium with a solution of sodium sulphite, and then filtering. On adding this solution to an alcoholic solution of benzyl chloride, a turbid liquid was obtained, which, however, soon cleared when heated on a water-bath under reflux. After a short time, sulphur dioxide was evolved, and a small quantity of a yellow oil separated, which, after removal from the remainder of the liquid, solidified on cooling; on re-crystallisation from alcohol, it was obtained in lustrous yellow crystals, melting at 90·5°, and had all the characteristic properties of dibenzyl diselenide, as described by Jackson (*Annalen*, 1875, clxxix., 1). It had probably been formed according to the following equations, the evidence for which the authors hope to publish later:—

$$C_6H_5{\cdot}CH_2Cl + Na_2SeSO_3 = C_6H_5{\cdot}CH_2{\cdot}Se{\cdot}SO_3Na + NaCl,$$

$$2C_6H_5{\cdot}CH_2{\cdot}Se{\cdot}SO_3Na + H_2O = (C_6H_5{\cdot}CH_2{\cdot}Se)_2 + Na_2SO_4 + H_2O + SO_2.$$

On allowing the mother-liquor to stand, a further quantity of diselenide slowly separated, sulphur dioxide being continuously evolved. The diselenide was also obtained from the mother-liquor, after the addition of potassium hydrogen carbonate, by electrolysis in a divided cell, the method being similar to that used in the preparation of disulphides (Price and Twiss, *loc. cit.*).

118. "*The Optical and Sensitising Properties of the* iso*Cyanine Dyes*." By SAMUEL EDWARD SHEPPARD.

The absorption spectra and sensitising power for gelatino-bromide plates have been investigated for a series of dyes of the *iso*cyanine group. It was shown that solutions in alcohol and chloroform conform to Beer's law, and that the colour is probably independent of ionisation. Further, in different solvents, the absorption follows Kundt's rule, the bands being shifted to the red as the dispersive power of the solvent increases. The influence of different substituted groups on the absorption and sensitising power was measured. It is found that for a group of dyes of similar chemical constitution the photo-chemical activity is proportional to the rate of fading in light. Comparison of the sensitising and absorption spectra shows that the bands in the latter are regularly displaced to the red some 10 $\mu\mu$, as would be expected from their behaviour in different solvents. The investigation of the conditions of sensitising by bathing shows that the "taking-up" of the dye is an absorption process comparable with substantive dyeing.

119. "*The Polarimetric Study of Intramolecular Rearrangement in Inactive Substances*." By THOMAS STEWART PATTERSON and ANDREW MCMILLAN.

Continuing previous work (*Trans.*, 1907, xci., 504; *Ber.*, 1907, xl., 2564), the authors have applied their new method for studying intramolecular re-arrangement in inactive compounds to measure the rate of inversion of piperonal-*syn*oxime at a number of temperatures. The increase of velocity with rise of temperature was found to obey van't Hoff's law. The method was also applied for the measurement of the inversion of *p*-iodobenz*syn*aldoxime in *n*-propyl tartrate, and to the transformation of *ω-iso*nitrotoluene into *ω*-nitrotoluene, satisfactory constants being obtained. It was shown that by the same method the dynamic isomerism of ammonium thiocyanate and thiocarbamide and of ammonium cyanate and carbamide could be followed.

120. "*Mercuric Zinc Cyanide*." (A Correction). By WYNDHAM ROWLAND DUNSTAN.

In a paper communicated to the Society in 1892 (*Trans.*, 1892, lxi., 666), the author described the results of an investigation of the "antiseptic cyanide" which had been introduced into surgery by Lord Lister. The conclusion was arrived at that the substance was an unstable double mercuric zinc cyanide, for which the formula proposed was $Zn_4HG(CN)_{10}$, and this was stated to correspond with 40·65 per cent of mercuric cyanide. This is a miscalculation, as the formula actually requires 35 per cent of mercuric cyanide, and must therefore be rejected.

The formula which most nearly corresponds with the maximum percentage of mercuric cyanide found, namely, 38·5, and which is also in accordance with the curves plotted from numerous experimental data, is $Zn(CN)_2,\frac{1}{2}HgCN)_2$, which requires 41·6 per cent of mercuric cyanide.

The salt, prepared as described, may therefore be regarded as a trizincic monomercuric octacyanide of the formula $Zn_3Hg(CN)_8$, which, as shown, inevitably suffers some decomposition by the water present during its precipitation.

121. "*Ethyl 6-Methyl-2-pyrone-3 : 5-dicarboxylate and its Derivatives*." By JOHN LIONEL SIMONSEN.

When ethyl ethoxymethylenemalonate reacts with ethyl sodioacetoacetate, *ethyl 6-methyl-2-pyrone-3 : 5-dicarboxylate* is obtained:—

$$(CO_2Et)_2{:}C{:}CH{\cdot}OEt + CHNaAc{\cdot}CO_2Et \rightarrow (CO_2Et)_2{\cdot}C{:}CH{\cdot}CHAc{\cdot}CO_2Et,$$

$$CH\begin{matrix}=C(CO_2Et){\cdot}CO_2Et \\ <C(CO_2Et){:}CMe{\cdot}OH\end{matrix} \rightarrow CH\begin{matrix}=C(CO_2Et)-CO \\ <C(CO_2Et){:}CMe\end{matrix}>O.$$

The same product results from the interaction of (I.) ethyl ethoxymethyleneaceteoacetate and ethyl sodiomalonate; (II.) ethyl ethoxymethyleneacetoacetate and the ethyl sodiocyanoacetate; and (III.) ethyl ethoxymethylene-cyanoacetate and ethyl sodioacetoacetate.

Ethyl 6-methyl-2-pyrone-3 : 5-dicarboxylate readily reacts with ammonia, with formation of *ethyl ammonium 6-hydroxy-2-methylpyridine-3 : 5-dicarboxylate*,—

$$CH\begin{matrix}=C(CO_2{\cdot}NH_4){\cdot}C(OH) \\ <C(CO_2{\cdot}E)-CMe\end{matrix}>N,$$

which on hydrolysis with alcoholic potash yields 6-hydroxy-2-methylpyridine-3 : 5-dicarboxylic acid,—

$$CH\begin{matrix}=C(CO_2H){\cdot}C(OH) \\ <C(CO_2H)-CMe\end{matrix}>N,$$

which has already been described by Errera (*Ber.*, 1900, xxxiii., 2969). The action of aniline on ethyl 6-methyl-2-pyrone-3 : 5-dicarboxylate has also been investigated.

122. "*Contributions to the Chemistry of the Amidines. Part II. 2-Anilinobenzoxazole and the supposed Anilodihydrobenzoxazole*." By GEORGE YOUNG and ALBERT EDWARD DUNSTAN.

The authors have re-investigated the two substances described in the literature as anilinobenzoxazole and anilodihydrobenzoxazole. They confirm the nature and constitution of the anilino-compound, but find that the supposed isomeride is in reality carbanilide.

The following substances were described:—

Acetylanilinobenzoxazole, $C_{13}H_9ON_2Ac$, m. p. 91°; *p-chlorophenylcarbamide*, $C_7H_7ON_2Cl$, m. p. 212°; di-*p*-chlorocarbanilide, m. p. 289°; *trichlorocarbanilide*, $C_{13}H_9ON_2Cl_3$, m. p. 262°; and di-*p*-tolylcarbamide, m. p. 265°.

123. "*The Slow Decomposition of Ammonium Chromate, Dichromate, and Trichromate by Heat*." By WALTER CRAVEN BALL.

When ammonium dichromate is heated at temperatures between 185° and 205°, it gradually becomes dark brown, and finally black, and nitrogen, water, and ammonia are evolved. After heating for several days, the remaining black substance has the approximate percentage composition:—Cr_2O_3, 83·89; active oxygen, 9·00; and water, 6·93. This corresponds fairly well with the formula $3CrO_2,H_2O$, but the composition is not quite constant.

If the heating is interrupted at an intermediate stage, it is found that part of the dichromate has decomposed, with production of a black insoluble substance, nearly half the nitrogen of the decomposed dichromate being contained in it. This black substance also varies in composition, but approximates to the formula $2CrO_3,Cr_2O_3,2NH_3,H_2O$.

The slow decomposition of ammonium dichromate is therefore partly a dehydration to this insoluble compound containing ammonia, and partly a combustion of the hydrogen of the ammonium to form water, with production of nitrogen.

The author has studied quantitatively the decomposition of ammonium chromate and of ammonium trichromate under similar conditions; the substances decompose in a similar manner.

FARADAY SOCIETY.

Ordinary Meeting, May 12th, 1908.

Mr. LEON GASTER in the Chair.

DR. F. MOLLWO PERKIN and Mr. L. O'DOWD read a paper on "*Determination of Boiling-points of very Small Quantities of Liquids*."

The determination of boiling-points of small quantities of liquids by distillation is not satisfactory, owing to the considerable loss which may take place, and also because of the difficulty of accurately arriving at the boiling-point before the liquid has distilled away. In the method described a small test-tube, made of thin glass, is passed through a hole in the cork in such a way that the end of it comes against the bulb of the thermometer. Through another hole a stirrer is passed. The heating vessel contains about 100 cc. of sulphuric acid or glycerin. About a quarter of a cc. of the liquid, the boiling-point of which

is to be determined, is placed in the small test-tube; this amount will rise nearly a centimetre up the tube. A small capillary tube, about 1 cm. long and sealed at one end, is dropped into this in such a manner that the open end rests upon the bottom of the test-tube. The external liquid is then heated fairly rapidly until a constant stream of bubbles is seen to rise from the end of the capillary tube. The source of heat is then removed, when the speed at which the bubbles are given off slackens, and, finally, when the last bubble makes its appearance and shows a tendency to suck back, the thermometer is immediately read. This is the boiling-point of the liquid, because it is the point at which the vapour pressure of the liquid is equal to the pressure of the atmosphere.

This method is really a modification of an older method, which, however, gives results which cannot be depended upon. The authors have determined the boiling-points of a large number of liquids and found the results to be perfectly accurate, both with low boiling-point substances such as ether and with high boiling-point substances such as safrol.

Mr. F. Mollwo Perkin read a paper entitled "*The Industrial Uses of Ozone, particularly in connection with Water Purification.*"

A brief account was first given of the various methods for obtaining ozone, and of the different processes employed for water purification and sterilisation. The method used by Siemens and Halske was then described in detail. The apparatus consists of two concentric electrodes, the inside one being of aluminium and the outside one of glass. The aluminium one, in order to keep it cool, is hollow and has water circulating through it. The external one is also kept cool by water contact, and as the water is in an iron container which is earthed, this acts as a negative pole, and of course water is a conductor on the high tensions which are employed. Dried air is passed up the annular space between the two electrodes, and, by means of the silent electric discharge which is there taking place, is ozonised. From the ozoniser the air passes up towers which are filled with pebbles, and over which the water trickles; by this means the water is divided up into a number of small streams, and consequently a very large surface is exposed to the action of the ozone. After the water has been thus treated it is allowed to flow into the reservoir in a series of cascades. By this means it comes in contact with the air, and any excess of ozone which may be in it is removed.

It is found that the water purified in this way becomes almost absolutely sterile, and any bacteria which may happen to remain are not of a pathogenic nature, consequently the water is absolutely safe for potable purposes.

Messrs. Siemens and Halske have a large installation for dealing with water at Wiesbaden and another for purifying the water supply at Paderborn.

They have also erected experimental plant in several other places. The process can be very cheaply carried out, as it does not cost more than ½d. for every cubic metre of water which is treated. A portable plant has also been devised and is of particular use in case of war; in fact, some of them were employed in the late Russo-Japanese war. They should also be of value for other purposes—if the water supply of any town were to become contaminated with typhoid, for example.

The paper finally discusses other uses for ozone, such as the oxidation of eugenol in the preparation of artificial vanilla and the bleaching and sterilising of flour, a process used in a very large number of mills in this country. Flour so sterilised is capable of export for long distances, and may be kept for a very long time without deteriorating.

Dr. T. M. Lowry thought that a simpler method of sterilising on a large scale was to soften the water and bring down the bateria in the precipitated chalk.

Dr. H. Borns pointed out that water from rapidly-flowing rivers needed little further purification.

Dr. G. Senter referred to the difficulties of removing the last traces of ozone from the sterilised water,

Dr. V. H. Veley remarked that germs that could not easily be destroyed were, as a rule, harmless.

The Chairman described an ozonising plant he had lately visited in Philadelphia, where the water purified was practically diluted sewage. This plant was capable of treating water for a population of 30,000, but occupied only thirty by fifty feet of ground, as against acres required for sand filters. He also gave some particulars of the Lahmeyer process.

Dr. V. H. Veley, F.R.S., exhibited an Apparatus for the Determination of the Dielectric Constants of Non-conducting Liquids.

In the usual bridge method balance is obtained by varying a resistance. In the author's apparatus a capacity is varied in such a way that variations are proportioned to the distance traversed by the movable condenser plate. These are read off directly, and a simple calculation gives the specific inductive capacity under measurement.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 17, April 27, 1908.

Ionisation of the Air by Ultra-violet Light.—Eugène Bloch.—Lenard has studied the ionising action of ultra-violet light upon gases, especially air, and has shown that the negative ions are small ions of high mobility, and the positive ions are large ions of low mobility. The Lenard effect appears to be a particular case of the Hertzian photo-electric effect. The author has experimented with different sources of ultra-violet light and with gases at rest and in motion, and has found that the greater part of the Lenard effect is attributable to the presence of photo-electric particles in suspension in the gas. When no dust is present the Lenard effect is much less marked than when dust is present.

Detection of Helium in Minerals containing Uranium.—F. Bordas.—Helium is very abundant, and seems to be combined with the uranium in samarskite, noegeite, euxenite, yttrotantalite, and anneroedite; less helium is found in woehlerite, pyrochlore, polycrase, troegerite, xenotime, gummite, thorite-orangite, and niobite-columbite. The minerals in which the salts of uranium are sharply defined or crystallised do not yield helium, *e.g.*, torbernite, autunite, carnotite. Helium has been detected by its line $\lambda = 5878$ in a sample of native bismuth from Saxony, and of bismuth with smaltine from Cornwall.

No. 18, May 4, 1904.

Carrying down of Soluble Substances by certain Precipitates.—Paul Frion.—In a basic medium more of a soluble substance is carried down by a precipitate than in a neutral medium, and more in a neutral than in an acid medium. The amount carried down increases as the concentration of the ion carried down increases, and also increases with the valency of the ion. The precipitate carries down most when it is in a dilute liquid. These different results can be interpreted by applying the laws of electrification by contact—thus the charge which each grain of the precipitate takes appears to be due to the ions H^{+ve} or OH^{-ve}, and is much diminished by the presence of polyvalent ions of opposite sign.

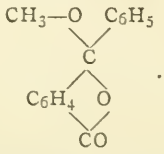
Determination of Halogens in Chloro-brominated Organic Compounds.—H. Baubigny.—The sulpho-chromic mixture can be used to determine chlorine and bromine in derivatives containing both halogens as follows:—The compound is treated with the mixture as

usual in presence of silver sulphate, and the volatile products are received in an alkaline solution of sulphite. The alkaline liquid must be divided into two equal parts. In one the chlorine and bromine are determined by precipitation, and in the other the alkali is neutralised, and after concentration the excess of sulphite is destroyed by potassium permanganate. The bromine is eliminated by drying *in vacuo* after the addition of copper sulphate and potassium permanganate. Thus the bromine is set at liberty, and the dry residue contains all the chlorine. The bromine can be calculated by difference.

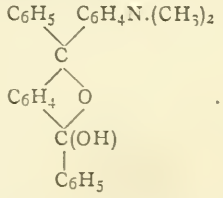
New Method of Preparing the Homologues of Naphthalene.—G. Darzens and H. Rost.—When α-acetylnaphthalene is led over reduced nickel, water-vapour and α-ethylnaphthalene are produced, $C_{10}H_7-CO-CH_3+4H = C_{10}H_7-CH_2-CH_3 + H_2O$. Under the same conditions β-acetylnaphthalene yields β-ethylnaphthalene, α-isobutyrylnaphthalene yields α-isobutylnaphthalene, and the β-iso-compound gives β-isobutylnaphthalene. These two last homologues of naphthalene had not previously been prepared.

Action of Phenyl Magnesium Bromide upon the Second Methyl Ether of Para-dimethylamido-orthobenzoyl Benzoic Acid.—J. Pérard.—Meyer has recently prepared the methyl ethers corresponding to the two tautomeric forms of orthobenzoyl-benzoic acid:—

$C_6H_4<\begin{matrix}CO-C_6H_5\\COOCH_3\end{matrix}$ and



By an analogous method the authors have obtained the second methyl ether of para-dimethylamido-orthobenzoyl-benzoic acid, and have found that the product obtained when phenyl magnesium bromide acts upon it is the same as when the first ether is used, *i.e.*:—



Fixation of Hydrocyanic Acid by Benzoyl Acrylic Acid.—J. Bougault.—Benzoyl acrylic acid and analogous compounds readily fix one molecule of hydrocyanic acid. The addition is made at the ethylene bond, and the acid obtained is α-cyanbenzoylpropionic acid, $C_6H_5-CO-CH_2-CH(CN)-CO_2H$. It appears to be identical with Klobb's phenacylcyanacetic acid. On saponification it yields β-benzoylisosuccinic acid, $C_6H_5-CO-CH_2-CH(CO_2H)_2$.

MISCELLANEOUS.

Central Technical College.—The Third Year Students of the Central Technical College are holding their Annual Dinner at the Gaiety Restaurant on Thursday, June 18, at 7.30 punctually. All Old Centralians are cordially invited to attend. Professor Dalby has kindly consented to preside. Tickets may be obtained from the Hon. Sec., C. H. RUSSELL, Ingram House, Stockwell, S.W., at 7s. each.

Infants' Health Exhibition.—This special Exhibition, under the auspices of the Incorporated Institute of Hygiene will be opened from the 15th to the 27th of June, at the Institute buildings in Devonshire Street, Harley Street, W., and is intended to demonstrate the progress and recent advances in connection with the health, comfort, and training of children. A most attractive and instructive display is assured, and as space is limited only those exhibits can be shown that represent merit or improvement and are of public interest. A great influx of visitors, in connection with various events, is expected in London between the 15th and 22nd of June, and such an Exhibition as this, held in the heart of the Metropolis, will be a source of interest, attraction, and education to many. It will appeal especially to mothers and heads of families, to medical men, matrons, and nurses, as well as to school teachers. The exhibits will represent and be shown in the following sections, viz.:—Foods, Clothing, the Nursery, the Bedroom, Recreation, Physical Exercise, School Life, Education.

MEETINGS FOR THE WEEK.

TUESDAY, 9th.—Faraday Society, 8. "Utilisation of Atmospheric Nitrogen in the Production of Calcium Cyanamide, and its Use in Agriculture and Chemistry," by Dr. A. R. Frank.

FRIDAY, 12th.—Physical, 8. "Experiments on a Directive System of Wireless Telegraphy," by Messrs. Bellini and Tosi. "Lateral Vibration and Deflection of Clamped Directed Bars," by Dr. Morrow. "On the Resistance of a Conductor of Uniform Thickness whose Breadth suddenly changes, and on the Shapes of the Stream-lines," by Prof. Lees. "Self-inductance of two Parallel Wires," by Dr. Nicholson. "Homogeneous Secondary Radiation," by Dr. Barkla and Mr. Sadler. "Notes on the Motion of a Corpuscle and on Cloud Formation," by Prof. Morton.

BIRMINGHAM MUNICIPAL TECHNICAL SCHOOL.

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The Council wish to draw special attention to the fact that the income arising from the Donation of the Worshipful Company of Goldsmiths is to be more or less especially devoted to the encouragement of Research in Inorganic and Metallurgical Chemistry. Furthermore, that the income due to the sum accruing from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the Coal-tar and allied industries.

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THE CHEMICAL NEWS.

VOL. XCVII., No. 2533.

NOTES ON GIESEL'S ARTICLE ON POLONIUM.

By W. MARCKWALD.

A RECENT number of the *Berichte* (1908, vol. xli., p. 1059; CHEMICAL NEWS, 1908, xcvii., 242) contains an article by Giesel on the preparation of polonium and its behaviour. Some statements in this article call for notice from me.

The second section begins with the statement that "The new precipitate is more active than deposits of polonium on metals." The separation of polonium as oxide (hydroxide) is not new, but was described by me three years ago (*Berichte*, 1905. xxxviii., 591). The three milligrms. of polonium separated from fifteen tons of pitchblende were obtained by specific reactions, which enable polonium to be separated from any known element. For this reason this polonium cannot have been appreciably impure, and cannot therefore be considerably inferior in activity to any other specimen. The effects of his preparation which Giesel mentions have almost all been observed by me in a polonium preparation which I exhibited in 1903 (*cf.*, *Berichte*, 1903, xxxvi., 2662) at the International Congress for Applied Chemistry, and which was about one-tenth as pure as the polonium afterwards obtained. I have repeatedly mentioned the strong ozonising power and the rapid destruction of the filter-paper (*cf.*, *Sitzungsbericht des Vereins für Gewerbefleiss*, Jan. 2, 1905).

The last sentence but one in Giesel's article reads, "No relationship to tellurium could be discovered." It is not clear what Giesel means by this sentence. The only "relationship" to tellurium which I assumed for polonium and which—it may prove to be true or not—served me excellently as a working hypothesis for the systematic preparation of polonium, consists in the position of polonium in the periodic system of the elements. After this hypothesis has served its purpose there is, of course, no reason for retaining it; but, on the other hand, in the observations which Giesel communicates I see not the least reason for rejecting it.—*Berichte*, 1908, xli., 1378.

THE ULTRA-VIOLET SPARK SPECTRUM OF DYSPROSIUM AND THE REMARKABLE MAGNETIC PROPERTIES OF THIS ELEMENT.

By G. URBAIN.

I. *Spectrum.*

THE only known spark spectrum of dysprosium is the visible spectrum obtained by Lecoq de Boisbaudran (*Comptes Rendus*, 1886, cii., 155) and containing only five nebulous lines, 583·5, 575·0, 570, 526·9, 525·9. This spectrum has been attributed to the element $Z\gamma$. Demarçay, moreover (*Comptes Rendus*, 1900, cxxxi., 388), has given some ultra-violet lines of dysprosium as characteristic of the element Δ.

The dysprosium, which I have obtained in a state of purity and which shows no variation in properties after systematic multiple fractionation, shows these lines very clearly, to the exclusion of other earths, and in the fractionations these lines behave like the absorption spectrum, by means of which Lecoq de Boisbaudran discovered and defined dysprosium.

There can be no doubt that these lines are as characteristic of the element as its absorption bands. Nevertheless, the knowledge of these lines appearing insufficient, I have made many more measurements with different photographs of the spark spectrum of dysprosium in the ultra-violet. This spectrum is one of the richest in lines of the family of the rare earths. In the following table only the principal lines are given, or those which are undoubtedly correct, for my apparatus did not enable me to take measurements which were precise enough to leave no doubt about the very faint lines.

The numbers in the following list are correct to two-tenths of an Angström unit:—

2872·0	Strong.	3498·8	
2904·1	Fairly strong.	3501·5	
2948·5	Fairly strong.	3504·5	
2950·4	Strong.	3506·8	
2955·4	Fairly strong.	3512·8	
2969·2	Strong.	3517·3	
3029·7		3524·2	Strong.
3038·4	Strong.	3527·3	
3052·3	Fairly strong.	3529·3	
3060·6	Fairly strong.	3531·9	Very strong.
3062·7	Fairly strong.	3535·1	Strong.
3109·8		3536·2	Strong.
3128·6	Fairly strong.	3538·5	Strong.
3135·5	Very strong.	3542·5	Fairly strong.
3140·7	Fairly strong.	3544·5	
3146·1		3546·8	
3152·4		3550·4	Strong.
3163·0	Strong.	3551·7	Strong.
3170·4		3574·0	
3206·5	Fairly strong.	3576·3	
3215·3	Strong.	3591·3	Fairly strong.
3216·7	Very strong.	3594·8	Fairly strong.
3221·5	Fairly strong.	3606·3	Fairly strong.
3223·3	Fairly strong.	3613·1	
3235·8	Strong.	3620·3	
3236·7	Fairly strong.	3630·5	Strong.
3245·3	Fairly strong.	3645·4	Very strong.
3251·5	Very strong.	3648·9	
3266·4	Very strong.	3695·0	Strong.
3309·0	Very strong.	3724·6	
3320·2	Strong.	3747·7	
3341·1	Strong.	3753·8	Fairly strong.
3385·9	Very strong.	3757·3	Strong.
3393·9	Very strong.	3786·3	
3396·3	Strong.	3788·6	
3420·0		3816·8	
3423·0		3872·3	Strong.
3434·7		3944·8	Very strong.
3439·1		3978·7	Fairly strong.
3445·7	Strong.	3997·0	
3447·2		4000·7	Strong.
3456·7	Fairly strong.	4045·7	Strong.
3461·1	Very strong.	4078·0	Strong.
3471·3	Strong.	4104·0	
3477·0	Strong.	4187·0	Fairly strong.
3494·6	Very strong.	4195·0	Fairly strong.
3496·5		4212·5	Very strong.
3498·0		4221·3	

This spectrum was obtained with solutions of the chloride, the spark being condensed.

II. *Magnetism.*

Stéphan Meyer (*Sitz. Ber. der R. Acad. zu Wien*, CX., 492) in 1901 published a certain number of magnetic measurements which he carried out with the rare earths fractionated by Cleve and by Nilson. Naturally no values are given for dysprosium in this note; dysprosium has only recently been isolated (G. Urbain, *Comptes Rendus* 1906, cxlii., 785), but under the heading "oxide of holmium" very high values of magnetic susceptibility are given.

From the publications of Cleve, his pupils, and the spectroscopists who examined their products I can easily

deduce what is the true nature of the substances called holmium. They are earths containing, besides yttrium and erbium and some other impurities, a notable proportion of true holmium, and possibly a still higher proportion of dysprosium; so much so that the values of $x \cdot 10^6$ obtained by Meyer for these substances have only a limited scientific value, in spite of the interest attached to them.

I have determined the coefficient of magnetisation of the oxides of dysprosium Dy_2O_3, obtained from consecutive members of one of my fractionations, by means of Curie and Chéveneau's magnetic balance. The following table gives the results of the experiments:—

No. of fraction.	Wt. of substance.	Deviation.	$x \cdot 10^6$.
31.	0·1974	26·27	289·5
32.	0·2031	26·77	286·9
33.	0·2256	29·98	289·3
34.	0·2796	37·48	291·7
35.	0·2476	33·03	290·4
36.	0·2491	33·23	290·4

Cobalt sulphate taken for comparison gave a deviation of 3·60 for 0·1974 grm. of sulphate. If the value $39{\cdot}7 \times 10^{-6}$ recently given by Meslin (*Ann. de Phys. et de Chim.*, 8th Series, 1906, vii., 182) is taken for the coefficient of magnetisation of this salt, we get for the different terms of this fractionation values lying irregularly between $286{\cdot}9 \cdot 10^{-6}$ and $291{\cdot}7 \cdot 10^{-6}$, *i.e.*, values which may be regarded as constant and of which the mean value is roughly $290 \cdot 10^{-6}$.

This high value gives dysprosium the first place amongst the paramagnetic elements. Its oxide Dy_2O_3 is about 12·8 times as magnetic as iron oxide Fe_2O_3.—*Comptes Rendus*, 1908, cxlvi., 922).

YTTRIUM EARTHS.*

First Paper.

By VICTOR LENHER.

The methods which we have at our disposal for the separation of the earths of the yttrium group may be classified under the following heads:—(1) Fractional precipitation; (2) Fractional crystallisation; (3) Fractional decomposition of such salts as the nitrates by heat.

Under fractional precipitation, we have methods which depend largely on the differences in basic properties, such as the fractional precipitation by ammonia, magnesia, &c. The speed by which separations are effected by use of this principle depends largely on how quickly the system can be brought into equilibrium.

In the methods of fractional crystallisation we must depend necessarily on the differences in solubility of various salts and as a rule with the mixtures which are found in the rare earth minerals; the solubilities of a given salt of the various metals are not widely different. On this account separation by the crystallisation of the nitrates or double nitrates is not rapid, while with the chromates accurate conditions must be observed, in which case this method gives splendid results.

The decomposition of the nitrates by heat is slow, but can, by patience, be carried out with success. The basic nitrate method of Welsbach (*Monatshefte*, v., 508) which can be applied to the yttrium group is a combination of this method and that of fractional precipitation. It is more rapid and successful than either method alone.

The successful use of any of the methods for separating the metals of the yttrium group depends largely on the ratios of the various constituents present in the mixtures, as well as on the character of the elements to be separated. We note, for example, that Dennis and Dales (*Journ. Am. Chem. Soc.*, xxiv., 428) in their study of the yttrium earths from sipylite find that magnesia, as a precipitating agent, causes little change in the atomic weights and absorption spectra, while James (*Ibid.*, xxix., 495) was more successful in using this method on gadolinite earths. James used the nitrate solution, while Dennis and Dales used a chloride solution. The author in working in a nitrate solution with yttrium earths from monazite has found that various fractions acted quite differently towards magnesia; some showed marked differences in atomic weight and absorption spectra after treatment with magnesia, while others showed little change. It has been observed, moreover, that in order to work this method with any appreciable degree of success the magnesia must be freshly ignited. The various degrees of success with different methods can also be illustrated by the Welsbach method (*Monatshefte*, xxvii., 935) of crystallising the oxalates from an ammoniacal solution or by the James method (*Journ. Am. Chem. Soc.*, xxix., 495) in which the "oxalate-carbonates" are crystallised from an ammonium carbonate solution of the oxalates. This method with gadolinite earths in the hands of James yielded first yttrium and successively fractions with higher atomic weight to ytterbium. In the author's hands, it has worked similarly with the yttrium earths from samarskite, but on applying the same method to certain oxalates from monazite, atomic weight determinations showed that the elements with heavier atomic weight appeared first, while the more soluble portion yielded fractions whose atomic weight was far below the more insoluble portions. In other words, we here have the same method producing opposite results with different mixtures of earths.

From time to time it has been proposed to use salts of organic acids. The oxalates can be crystallised from either ammoniacal or ammonium carbonate solution, yielding a fairly rapid method of fractionation, or the oxalates can be crystallised from nitric acid solution, yielding fractions of different atomic weights. The ethyl sulphates and the acetyl acetonates have been used by Urbain and others as means of separation in this group. The formates have been repeatedly used for fractionations. Salts of a number of organic acids have been prepared, but little has been done in the application of the derivatives as means of separation. Such salts as the tartrates, citrates, and succinates have been prepared, but little has been attempted in the way of separation.

The tartrates and citrates of the yttrium earths appear as white gelatinous precipitates when a neutral salt of potassium, sodium, or ammonium is added to a solution of the yttrium salt. In a similar manner insoluble derivatives are formed with neutral salts of fumaric, maleic, tartronic, malic, and malonic acids. The neutral succinates of the alkalis or ammonium deport themselves in a very interesting manner with the neutral nitrates of the yttrium earths.

When neutral ammonium or sodium succinate is added to a neutral nitrate solution of the yttrium earths and the solution allowed to stand, a finely divided crystalline precipitate forms slowly; in fact, in the cold a few hours are necessary to insure complete precipitation. On the other hand, when the solution is hot or boiling, complete precipitation is effected in much less time, from ten minutes to half-an-hour being sufficient time for complete formation of the insoluble succinates. The ready formation of this finely divided precipitate and the fact that the reaction is far from instantaneous appears to us as promising to be a satisfactory method for fractionation. The fact that it forms as slowly as it does would indicate that there should be plenty of time for equilibrium to be established, and the physical character of the salt and its insolubility enables it to be quickly filtered and readily washed.

That the yttrium earths form succinates was shown by Berlin in 1835 (*Pogg. Ann.*, xliii., 108). He showed that with sodium succinate the yttrium earths form a fine crystalline powder. Ekeberg in 1802 (*Gilb. Ann.*, xiv., 247; *Ann. Chim. Phys.*, xliii., 228) thought that the yttrium earths were not precipitated by the alkaline succinates, while beryllium was, which was contrary to the

results found by Berlin and to the work of Cleve and Höglund (*Ber.*, vi., 1468) who showed that ammonium succinate precipitates yttrium but not erbium from nitrate solution, but out of a mixture precipitates both.

In the thorium cerium group, Berzelius showed in 1829 (*Pogg. Ann.*, xvi., 385) the formation of an insoluble succinate of thorium. This reaction has been later studied by Kaufmann (Dissertation Rostock University, 1899) and Schilling (Dissertation Heidelberg University, 1902, p. 141). The use of an alkaline succinate has been recommended as a means of separation of iron from the gadolinite earths by Gadolin, Vauquelin, Berzelius, Berlin, and Hermann, after Klaproth had shown that iron would be first precipitated from such a solution.

The yttrium earths from samarskite have been studied with the view of testing the applicability of the succinates as a means of separation in this group.

Treatment of Samarskite.

Fifteen pounds of samarskite containing very little gangue minerals were treated with concentrated hydrofluoric acid according to the method of J. Lawrence Smith. The mineral dissolved with effervescence. The columbium and tantalum passed into solution, while the earths appeared as insoluble fluorides. These insoluble fluorides were thoroughly washed with water by decantation, after which they were dried and treated with concentrated sulphuric acid. After the first copious evolution of hydrofluoric acid, the mass was warmed and finally heated until the heavy fumes of the sulphuric acid came off. The pasty mass was allowed to cool; when it was extracted with water, and the insoluble residue, which consisted of more or less of the oxides of columbium and tantalum, insoluble sulphates, and a little undecomposed mineral, was thoroughly washed with water by decantation. This sulphate solution of the earths and uranium was nearly neutralised with sodium hydroxide. Oxalic acid was then added, and the oxalates precipitated. These crude oxalates were ignited to oxides, dissolved in nitric acid, and treated with a hot saturated solution of potassium sulphate, with the addition of the sold salt. The soluble yttrium double sulphate solution was precipitated with oxalic acid, the oxalates were roasted to oxides, from the nitric acid solution of which it was again treated with potassium sulphate. Three such treatments with potassium sulphate from the nitrate solution were found necessary to completely remove the more insoluble group of earths, and after three such treatments the didymiums could not be detected in a strong solution of the nitrates by means of their characteristic absorption spectra, nor could cerium be detected by means of hydrogen peroxide.

Fractionation of the Succinates.

(With R. C. Benner).

About one hundred grms. of the oxides were dissolved in nitric acid and the slight excess of free acid neutralised in ammonia. This neutral nitrate solution was diluted to a litre, brought to boiling, and a saturated solution of neutral sodium succinate added in portions of 100 cc. By this means twelve fractions were obtained. After the addition of each portion of the sodium succinate, the solution was boiled fifteen minutes, after which the succinates were filtered and washed with 400 cc. of hot water. The fractions thus obtained were dried and ignited to oxide, small portions being taken for the determination of the atomic weight and the study of the absorption spectra.

The fractions thus obtained were combined and refractionated, selection being made of the portions whose atomic weights were close to each other; thus, for the second series, 2, 3, and 4 were combined, and 5, 6, 7, and 8 were united, while the lightest material, 9, 10, and 11, was similarly combined.

These oxides were dissolved in nitric acid, the excess of nitric acid removed by evaporation and in a dilution similar to that in Series I. were fractionated by addition of sodium succinate in fractions as before. By again combining fractions of close atomic weight in three such series of fractionations the most soluble succinate fraction gave a nearly white oxide, whose nitrate solution showed only very weak absorption bands. The atomic weight of the element in the most soluble portion was 93, and the fraction corresponds to yttrium containing small amounts of samarium, europium, and holmium as shown by the absorption spectra.

Series I.

	Weight of fraction as oxide. Grms.	Atomic weight in R_2O_3.
1.	22·2	114·2
2.	15·8	111·83
3.	10·0	110·06
4.	8·8	111·30
5.	9·0	108·5
6.	7·1	107·2
7.	7·0	105·6
8.	6·1	104·4
9.	7·0	101·0
10.	6·4	97·0
11.	4·0	95·8
12.	3·0	—

On the other hand, the third fraction at the other end of the series or the most insoluble portion gave a yellow earth whose atomic weight corresponded to 139. This oxide dissolved in nitric acid to a pink solution and showed absorption bands, and was doubtless a mixture of yttrium with terbium, holmium, europium, samarium, and erbium. Further study of these earths is being continued.

It has been considered well worth the while in making these studies on the samarskite earths and on the work which is in progress on the yttrium earths from monazite to determine the atomic weight in each fraction and also to study the absorption spectra.

The determination of the atomic weight for control purposes can be carried out sufficiently accurately by the estimation of the oxalic acid and of the earth oxide in the oxalate. While it is true that this method has some serious defects, yet very good results can be obtained if it is properly handled.

Baxter (*Journ. Am. Chem. Soc.*, xxviii., 1684) has recently shown in splendid detail that when the oxalates of neodymium, praseodymium, yttrium, and certain other of the rare earths are precipitated in neutral or nearly neutral solution, they exhibit a strong tendency to carry down ammonium oxalate. This carrying down of ammonium oxalate by the insoluble oxalates of the yttrium earths is very pronounced and is difficult to prevent without going to the opposite extreme and making the solution too acid, in which case we have the factor of the solubility of the oxalate in acid appearing and the obviously incomplete precipitation of the oxalate. In the first case, the result due to the presence of additional oxalic acid in the precipitated oxalate would cause the atomic weight to be too low, while if considerable free nitric acid is present, the more soluble yttrium oxalate is incompletely precipitated, and the result is to obtain a high atomic weight, due to the greater solubility of yttrium oxalate in nitric acid than of those earths of higher atomic weight.

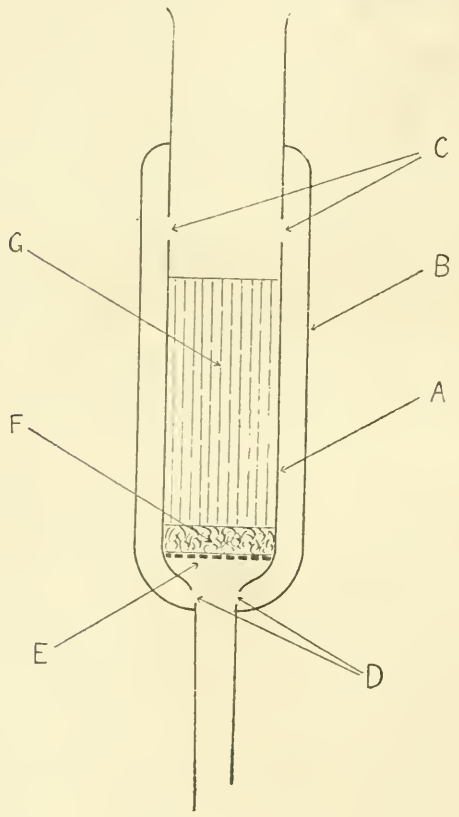
The most accurate method for the precipitation of the oxalate of the yttrium earths which has come to the attention of the author has been to use a grm. or less of the nitrate in very slightly acid solution and to use a dilution of about 500 cc. The oxalate is precipitated from the boiling solution by means of a dilute solution of pure oxalic acid.

In conclusion, the author wishes to acknowledge his appreciation of the courtesy of Mr. H. S. Miner, of the Welsbach Co., of Gloucester, N.J., who has placed at our disposal a large quantity of rare earth residues from Carolinian monazite, and who has been able to secure for us a quantity of rare minerals for the study of the chemistry of the metals of the yttrium group. — *Journal of the American Chemical Society*, xxx., No. 4.

AN APPARATUS FOR SIMULTANEOUSLY EXTRACTING A SOLID AND FILTERING THE SOLUTION SO OBTAINED.

By FREDERICK RECORD, B.Sc.

THE apparatus, shown in section in the accompanying figure, was designed to obviate the loss of substance which occurs in the course of filtration subsequent to the extraction of solids with such solvents as ether and alcohol. It consists or an inner tube, A, sealed to a shorter concentric jacket, B. In that portion of A which is within B there are two pairs of holes, C and D. The apparatus is prepared for use by inserting in A a filter disc, E, and covering this, first with one or two pieces of filter-paper, and then with a layer, F, of asbestos. Above the latter is



placed the substance, G, which is to be extracted. A reflux condenser is attached to the upper part of the apparatus, and a flask containing the solvent to the lower end. On boiling the solvent its vapour rises through the apertures at D into the annular space between A and B, from whence it passes through C into A again, and finally into the condenser. The liquid formed by condensation drops on to G and percolates through it, dissolving a little on the way. The solution thus obtained falls through F and E and is filtered by them. This process continues until the whole of the soluble material has passed into the flask.

The Technical College,
Derby.

THE SEPARATION OF MAGNESIUM FROM THE ALKALIS BY ALCOHOLIC AMMONIUM CARBONATE.

By F. A. GOOCH and ERNEST A. EDDY.

NEARLY fifty years ago Schaffgotsch (*Ann. Phys.*, 1858, civ., 482) brought out the ammonium carbonate method for the separation of magnesium from the alkalis. According to this process, the very concentrated solution of the sulphates, nitrates, or chlorides of magnesium, sodium, and potassium is treated with a concentrated solution of ammonium carbonate. The voluminous precipitate which first falls is acted upon by an excess of the precipitant, sometimes dissolving completely, and crystalline ammonium magnesium carbonate, $MgCO_3.(NH_4)_2CO_3.4H_2O$, is soon formed. After standing twenty-four hours the precipitate is filtered off, washed with the concentrated ammoniacal solution of ammonium carbonate, dried, and strongly ignited. In the absence of salts of potassium, the residue is weighed at once as magnesium oxide, and from the filtrate sodium salts are recovered by evaporation. When a salt of potassium is originally present, with or without a salt of sodium, the ignited magnesium oxide is to be washed out, and again ignited before weighing, and the washings are to be added to the filtrate containing the greater part of the alkalis.

When Schaffgotsch published this method it was customary to deal in analysis with larger amounts of material than at present, and the requirements as to results were not so exacting. (A similar method was published by H. Weber, *Jahresb. Chem.*, 1858, p. 606). In eight complete determinations, upon which Schaffgotsch rested, weights of salts taken ranged between 1·75 grms. and 3·69 grms., and the magnesium oxide taken approximated 0·6 grm.; while the error in the weight of magnesium oxide found varied from 0·0007 grm. to 0·0082 grm., with an average error amounting to 0·6 per cent.

Though these results do not meet the modern requirements of a good analytical method, the process has been recently recommended and applied in rock analysis by Wuelfing (*Ber.*, 1899, xxxii., 2214), and mentioned by Hillebrand (*Bull.* 305, 149, U.S. Geol. Survey). It has seemed to us desirable therefore that the method should be again submitted to careful testing, and to that end the following work was undertaken.

Experimental.

Schaffgotsch's reagent was prepared by dissolving 230 grms. of ammonium carbonate in 180 cc. of ammonium hydroxide, diluting the solution to 1 litre, and filtering.

A solution of magnesium chloride was prepared by the following process:—Presumably pure magnesium oxide, 20 grms., was treated with nitric acid not quite sufficient in amount to act upon all the oxide. The solution thus obtained was diluted somewhat, and boiled and filtered to remove traces of the elements of the iron group. From this filtrate the greater part of the magnesium was precipitated by concentrated ammonium carbonate, thrown upon a filter, washed, and nearly dissolved in nitric acid. The solution, containing some undissolved magnesium carbonate, was first boiled and filtered to remove traces of the elements of the calcium group, and then treated again with ammonium carbonate to precipitate magnesium carbonate. The insoluble magnesium carbonate was washed and dissolved in the least possible amount of hydrochloric acid; and the solution was suitably diluted, and standardised by heating definite portions in a large platinum crucible with sulphuric acid, evaporating, removing the excess of sulphuric acid by careful heating over a radiator, and bringing to constant weight the residue of magnesium sulphate. With the Schaffgotsch reagent and the standard solution of pure magnesium chloride the following experiments were made:—

In Table I. are given results of experiments made to test the solubility of the ammonium magnesium carbonate in an

TABLE I.

MgO taken as $MgCl_2$. Grm	MgO weighed. Grm.	Error MgO. Grm.	MgO found as $Mg_2P_2O_7$ in filtrate. Grm	Volume of precipitant. Cc.	Volume of reagent used in washing. Cc.
		A.			
0·0029	—	−0·0029	0·0024	100	—
0·0289	0·0286	−0·0003	0·0007	10	—
0·1444	0·1430	−0·0014	0·0006	50	—
0·1444	0·1427	−0·0017	0·0009	50	50
		B			
0·0034	—	−0·0034	0·0033	100	—
0·0342	0·0342	—	0·0002	10	—
0·1708	0·1694	−0·0014	0·0012	50	—
0·1708	0·1696	−0·0012	0·0012	50	—
0·1708	0·1698	−0·0010	0·0020	50	25
0·1708	0·1683	−0·0025	0·0024	100	10
0·1708	0·1670	−0·0038	0·0043	200	10

TABLE II.

MgO taken as $MgCl_2$. Grm.	MgO weighed. Grm.	Error in MgO. Grm.	MgO found as $Mg_2P_2O_7$. Grm.	Original volume. Cc.	Volume of alcohol added. Cc.	Volume of precipitant. Cc.	Volume of solution used in washing. Cc.
			A.				
0·1444	0·1446	+0·0002	0·0001	—	—	50	—
0·1444	0·1449	+0·0005	—	—	—	100	—
0·1444	0·1445	+0·0001	—	—	—	100	50
0·1444	0·1445	+0·0001	—	—	—	100	50
			B.				
0·1444	0·1443	−0·0001	—	50	50	50	—
0·1444	0·1440	−0·0004	0·0002	50	50	50	—

TABLE III.

MgO taken. Grm.	NaCl taken. Grm.	KCl taken. Grm.	NH_4Cl taken. Grms.	MgO weighed. Grm.	Error MgO. Grm.	MgO found as $Mg_2P_2O_7$. Grm.	Volume of water solution. Cc.	Volume of alcoho added. Cc.	Volume of precipitant. Cc.	Volume of solution used in washing. Cc.	Time of standing.
					A.						
0·1444	—	0·1	—	0·1455	+0·0011	—	1—2	—	100	50	Over night
0·1444	0·1	—	—	0·1446	+0·0002	—	1—2	—	100	50	„
					B.						
0·1444	—	0·1	—	0·1445	+0·0001	0·0001	50	50	50	50	20 minutes
0·1444	—	0·1	—	0·1444	—	0·0001	50	50	50	50	20 „
0·1444	0·1	—	—	0·1445	+0·0001	0·0002	50	50	50	50	20 „
0·1444	0·1	—	—	0·1449	+0·0005	0·0001	50	50	50	50	20 „
0·1444	0·2	—	—	0·1449	+0·0005	0·0002	50	50	50	50	20 „
0·1444	—	0·2	—	0·1461	+0·0017	—	50	50	50	50	20 „
0·1444	—	—	3·0	0·1444	—	0·0001	50	50	50	50	20 „
0·1444	—	—	3·0	0·1447	+0·0003	0·0002	50	50	50	50	20 „
					C.						
0·1444	0·2	—	—	0·1446	+0·0002	0·0002	50	50	50	50	20 „
0·1444	—	0·2	—	0·1442	−0·0002	0·0002	50	50	50	50	20 „

excess of the precipitant of full strength or half strength. Definite portions of the standard solution of magnesium chloride were evaporated in a beaker of 250 cc. capacity nearly to dryness, and the precipitant was added in the amount indicated. The mixture, stirred vigorously until the flocky precipitate had disappeared, and the crystalline double carbonate had begun to form, was allowed to stand at least twenty-four hours. The precipitate, filtered off on asbestos in a perforated crucible, the filtrate being used to effect the transfer without addition of other liquid, was dried, ignited, and weighed as magnesium oxide. The filtrate was treated with microcosmic salt, and, after standing over-night, was again filtered on asbestos in a weighed perforated crucible, and the precipitate was washed with water faintly ammoniacal, dried, ignited, and weighed. The increase in weight of the crucible was taken as magnesium pyrophosphate from which the magnesium oxide was calculated. In the experiments of A, Schaffgotsch's reagent of full strength was used as the precipitant. In B the same reagent was used of half strength.

These experiments show plainly that ammonium magnesium carbonate is noticeably soluble in Schaffgotsch's solution of full strength, and rather more so in the same reagent of half strength. So, it is evident that an exact separation of magnesium from the alkalis, in solutions of reasonable volume, cannot be made without some modification of the method. The effect of adding to the mixture certain proportions of alcohol was therefore tried, and, after some preliminary attempts, a series of experiments was performed for which the precipitant used was made by saturating with ammonium carbonate a mixture of 180 cc. of ammonium hydroxide, 800 cc. of water, and 900 cc. of absolute alcohol, and filtering, after some hours, from the undissolved ammonium carbonate. In the experiments of Table II. (A), portions of the standard solution of mag-

nesium chloride were evaporated nearly to dryness, and to the residue was added a definite amount of the alcoholic solution of ammonium carbonate. The precipitates, after stirring and standing over-night, were filtered upon asbestos in the perforated platinum crucible, washed with the precipitant, dried, ignited strongly, and weighed. The filtrates were examined as before for dissolved magnesium by the phosphate method. In the experiments of Table II. (B) an equal volume of alcohol was added to the solution of magnesium chloride taken, and to this mixture was added, as a precipitant, a volume of the saturated alcoholic solution of ammonium carbonate equal to that of the magnesium chloride. The precipitate was filtered, washed, dried, ignited, and weighed as in the former experiments. The filtrate was examined as before for magnesium.

From the results of Section A of this table, it appears that the precipitation of the magnesium brought about in 100 cc. of a saturated ammoniacal ammonium carbonate solution containing 50 per cent of alcohol is complete. From the result of Section B it appears that the precipitation produced in 150 cc. of a one-third saturated solution of ammonium carbonate containing 50 per cent of alcohol is reasonably complete.

Table III. shows the details of certain experiments in which the separation of magnesium from the alkalis was attempted by the precipitation processes of Table II. In the experiments of A the precipitation was brought about by treating the solution of magnesium chloride and the alkali chlorides, concentrated in the highest degree, with the saturated ammoniacal ammonium carbonate solution containing 50 per cent of alcohol. In the experiments of B an equal volume of absolute alcohol was added to the water solution containing magnesium chloride and the alkali chlorides, and to this mixture was added the saturated ammoniacal ammonium carbonate solution containing 50 per cent of alcohol. In the experiments of C the precipitate was made as in the experiments of B, but, after pouring off the supernatant liquid through the asbestos felt of a weighed perforated platinum crucible, was dissolved in the beaker by warming with the least possible amount of hydrochloric acid. The solution was diluted with water to 50 cc., and treated as in the first precipitation. The second precipitate was collected upon the asbestos felt through which the supernatant liquid had been filtered after the first precipitation, ignited, and weighed. The filtrates were tested for dissolved magnesium as in former experiments. In experiments in which the filtration was made after twenty minutes it was found advisable to hurry the crystallisation by stirring the mixture for not less than five minutes after adding the precipitant.

The results of each method of treatment are plainly very good, but it is more convenient to add alcohol to a water solution than to evaporate a solution, and then treat the residue. Re-precipitation is shown to be advisable when large amounts of the alkalis are present. For amounts comparable to those which we have handled, the procedure is very rapid and simple. The solution containing the salts of magnesium and the alkalis is brought to a volume of about 50 cc., and an equal amount of absolute alcohol is added, precipitation is made by addition of 50 cc. of the saturated ammoniacal ammonium carbonate solution containing 50 per cent alcohol, and the mixture is allowed to stand twenty minutes with stirring for five minutes. If the amount of alkali salt originally present is small, the precipitate may be collected on asbestos in a perforated crucible, washed with the precipitant, dried, ignited, and weighed as magnesium oxide. When the amount of alkali salt originally present is large, the precipitate may be freed from traces of the alkali salt by pouring off the supernatant liquid through the prepared asbestos filter, dissolving the precipitate, and precipitating ammonium magnesium carbonate as at first. This second precipitate, collected upon the filter originally used, leaves upon ignition practically pure magnesium oxide.—*American Journal of Science*, xxv., p. 444.

THE DETERMINATION OF BENZENE IN ILLUMINATING GAS.*

By L. M. DENNIS and ELLEN S. McCARTHY.

I. *The Absorption of Benzene by Ammoniacal Nickel Nitrate.*

In 1903 Dennis and O'Neill described an absorption method for the determination of benzene in illuminating gas (*Journ. Am. Chem. Soc.*, xxv., 503). The absorbent there recommended was an ammoniacal solution of nickel nitrate, the use of such a solution for the determination of benzene having been suggested by the statement of Hofmann and Küspert (*Zeit. Anorg. Chem.*, 1897, xv., 204), that when illuminating gas acts upon a mixture of nickel hydroxide and ammonia, there is formed a compound of nickel cyanide with ammonia and benzene, $Ni(CN)_2.NH_3.C_6H_6$.

In practice, this method for the determination of benzene in some localities has given most excellent results, while in other quarters it has been far from satisfactory. Morton recently demonstrated that when mixtures of *benzene and air* are analysed with the use of the reagent (*Journ. Am. Chem. Soc.*, 1906, xxviii., 1728), the results are scarcely better than might be obtained with water alone, and that, moreover, the efficiency of the absorbent steadily decreases as the amount of benzene that it has taken up increases. These statements of Morton have been substantiated in this laboratory, and the only explanation of the excellence of the results in the analyses of mixtures of air and benzene as published by Dennis and O'Neill would seem to lie in the fact that but few absorptions of benzene were made, and that, consequently, the reagent had not taken up sufficient benzene to render the loss in its absorbing power noticeable.

Confronting the facts adduced by Morton, however, were arrayed statements from several University and technical laboratories testifying to the satisfactory character of the method and the uniformity of results obtained by it in analyses of illuminating gas. In seeking for explanation of these variations in the reports of different chemists it occurred to the authors of the present paper that those samples of illuminating gas on which the method gave good results might have contained cyanogen compounds necessary to the formation of the compound that Hofmann and Küspert described, while the poor results on other samples of illuminating gas might be caused by the absence of cyanogen compounds from the gas. To test the validity of this assumption, the ammoniacal nickel nitrate solution recommended by Dennis and O'Neill was used in a series of analyses of a gas mixture containing benzene, hydrocyanic acid, and air.

The hydrocyanic acid gas for these analyses was prepared by filling a Hempel nitrometer with mercury, then introducing from five to ten cubic centimetres of a concentrated solution of potassium cyanide, and adding gradually through the side arm about the same volume of hydrochloric acid (one part of acid to one part of water). The gas set free by this reaction was completely absorbable by caustic potash. It probably contained small amounts of cyanogen and carbon dioxide, but it will be referred to below as "hydrocyanic acid." A mixture of this gas with benzene and air was obtained by measuring off a volume of air, then passing this into a Hempel simple gas pipette containing liquid benzene, drawing the gas back into the burette and noting the increase in volume, and finally drawing into the burette the hydrocyanic acid gas that had been evolved in the nitrometer, and again measuring the volume. The measurements were made in a jacketed Hempel gas burette with mercury as the confining liquid. Several mixtures prepared in this manner were analysed by the Dennis and O'Neill method. The same sample of ammoniacal nickel nitrate was employed for all of the absorptions listed in Tables I., II., and III.

* From the *Journal of the American Chemical Society*, xxx., No. 2.

Table I. gives the results obtained with the mixture of air, benzene, and hydrocyanic acid. The completeness of the absorption may be seen by comparing the volume of air taken with the volume of gas remaining after absorption. It will be noted that the agreement is practically exact in every case except the fourth.

TABLE I.

No. of experiment.	Air taken.	Benzene taken.	Hydrocyanic acid gas taken.	Volume remaining after absorption by ammoniacal nickel nitrate.
	Cc.	Cc.	Cc.	Cc.
1.	56·2	1·0	3·2	56·2
2.	56·4	0·6	2·4	56·5
3.	56·5	1·9	2·4	56·5
4.	56·8	3·4	5·5	57·1
5.	57·7	1·5	1·2	57·7
6.	58·1	1·4	1·5	58·1
7.	58·2	2·1	6·1	58·3
8.	59·1	0·8	1·3	59·1

While the above table demonstrates that, in the presence cyanogen compounds, ammoniacal nickel nitrate quantitatively absorbs benzene vapour, the accurate results obtained by some analysts with the reagent could even yet not be explained, if these cyanogen compounds in a gas mixture are completely removed by potassium hydroxide, the reagent that precedes the ammoniacal nickel nitrate in the analysis of illuminating gas. To ascertain whether any of the cyanogen compounds are left in the gas mixture after it has been passed into the potassium hydroxide pipette, the analyses given in Table II. were made. In each analysis the gas mixture was allowed to remain in the potassium hydroxide pipette for such a length of time as had been found to suffice for the absorption of all of the hydrocyanic acid when that was mixed with air alone. The results show that when hydrocyanic acid, benzene, and air are present together, potassium hydroxide does not remove all of the hydrocyanic acid, the benzene appearing to exert a deterrent effect upon the absorption. It will be noted that the ammoniacal nickel nitrate quantitatively removed the benzene and the residual hydrocyanic acid in nearly every case.

TABLE II.

No. of expt.	Air taken.	Benzene taken.	Hydrocyanic acid gas taken.	Volume absorbed by potassium hydroxide.	Volume absorbed by ammoniacal nickel nitrate.	Volume remaining after absorption by ammoniacal nickel nitrate.
	Cc.	Cc.	Cc.	Cc.	Cc.	Cc.
9.	59·4	1·4	7·2	6·9	1·7	59·4
10.	59·9	0·5	8·6	8·4	0·5	60·1
11.	60·2	1·1	3·1	3·0	1·1	60·3
12.	56·1	0·9	5·5	4·8	1·6	56·1
13.	56·4	0·9	1·7	1·6	1·0	56·4
14.	56·7	1·3	2·0	1·8	1·5	56·7
15.	57·0	0·7	14·3	13·1	1·8	57·1
16.	57·8	1·7	1·9	1·9	1·7	57·8

If, from the results in the above table, we are justified in assuming that after treatment with caustic potash some cyanogen compounds still remain in illuminating gas, it at once becomes evident why the Dennis and O'Neill method gave satisfactory results with such samples of illuminating gas as contained cyanogen compounds.

After the first three determinations in Table II. had been made, it was thought possible that the ammoniacal nickel nitrate had then taken up sufficient hydrocyanic acid to enable it to absorb benzene vapour without the addition of further hydrocyanic acid gas to the mixture. This assumption seems also to be borne out by the fact that in Derminations 11 and 13 the absorption of benzene was complete even when only 1/10 of a cubic centimetre of "hydrocyanic acid" gas was present with the benzene vapour. The results of these analyses are given in Table III.

TABLE III.

No. of experiment.	Air taken.	Benzene taken.	Volume absorbed by ammoniacal nickel nitrate.
	Cc.	Cc.	Cc.
17.	60·5	1·5	1·5
18.	60·5	1·9	1·8
19.	60·9	0·9	0·7
20.	60·8	1·4	1·4
21.	61·2	0·7	0·7

The results, Nos. 12 to 21 inclusive, demonstrate that after the ammoniacal nickel nitrate has taken up some cyanogen it is able quantitatively to absorb fairly large amounts of benzene vapour, and that if cyanogen compounds are present in illuminating gas, the benzene content may accurately be determined by the method of Dennis and O'Neill. If, however, the reagent contains no cyanogen compounds, and if none are present in the gas that is being analysed, the method will not give accurate results.

II. *The Absorption of Benzene by Ammoniacal Nickel Cyanide.*

The foregoing experiments having demonstrated that a solution of ammoniacal nickel nitrate cannot be relied upon for the absorption of benzene from all samples of illuminating gas, the necessity arose for such modification of the method as would render it uniformly accurate.

It is apparent that to insure complete absorption of the benzene from all gas mixtures through the formation of the ammonia benzene nickel cyanide, cyanogen must be present in every case. This led to the use of an ammoniacal solution of nickel cyanide as an absorbent in place of the ammoniacal solution of nickel nitrate (see also Hofmann and Arnoldi, *Ber.*, 1906, xxxix., 339).

Preparation of the Ammoniacal Solution of Nickel Cyanide.—To 50 grms. of nickel sulphate ($NiSO_4.7H_2O$), dissolved in 75 cc. of water, are added 25 grms. of potassium cyanide dissolved in 40 cc. of water. After the addition of 125 cc. of ammonium hydroxide (sp. gr. 0·91) the mixture is shaken until the nickel cyanide has completely dissolved, and is then allowed to stand at a temperature of 0° for twenty minutes. The clear liquid is decanted from the crystals of potassium sulphate that have been precipitated, and is treated with a solution prepared by dissolving 18 grms. of crystallised citric acid in 10 cc. of water. After the mixture has stood again at 0° for ten minutes, the greenish blue supernatant solution is decanted and is introduced into a gas pipette. Two drops of liquid benzene are now added to the reagent through the large tube of the pipette, and the pipette is shaken until the benzene has combined with the reagent. This is effected in two or three minutes. This addition of benzene to the reagent is made because it was found that at times a freshly prepared solution of the ammoniacal nickel cyanide did not quantitatively remove benzene vapour until it had been used for four or five determinations and had absorbed some of the substance. Hofmann and Arnoldi used acetic acid in the preparation of the absorbent. This we have replaced by citric acid because of the appreciable vapour tension of acetic acid at ordinary temperatures.

Apparatus Employed.—The reagent was placed in a Hempel gas pipette of the form used for the absorption of heavy hydrocarbons by means of fuming sulphuric acid, the upper bulb that is filled with broken glass being, however, 4·6 cm. in diameter, which is somewhat larger than in the usual Hempel pipette. The measurements of the gas volumes were made in a Hempel gas burette provided with a water jacket, and if changes of temperatures occurred corrections were made for them. Numerous experiments showed that satisfactory results may be obtained with either water or mercury as the confining liquid in the burette.

Analytical Procedure.—After the sample of gas has been measured in the burette, the burette is connected by means of the usual capillary tube with a pipette containing the ammoniacal nickel cyanide solution, and the gas mixture is repeatedly passed over into the pipette and drawn back into the burette for a period of about two minutes. The pipette is then disconnected and the gas is passed into a "fuming sulphuric acid" Hempel gas pipette containing a 5 per cent solution of sulphuric acid, this being done to remove the ammonia that enters the gas mixture from the reagent. The ammonia is not easily absorbed by the dilute sulphuric acid, and the gas mixture must, consequently, be passed into and withdrawn from the pipette repeatedly for about two minutes to effect its complete removal.

Experimental Results.—The experiments that were made to ascertain the applicability of the reagent to the absorption of benzene and the accuracy of the method may be classified under the following heads:—

(1) Determination of Benzene in Known Mixtures of Benzene and Air;

(2) Study of the Behaviour of an Ammoniacal Solution of Nickel Cyanide toward Known Mixtures of Ethylene and Air;

(3) The Determination of Benzene in Coal Gas;

(4) The Determination of the "Analytical Absorbing Power" of the Ammoniacal Solution of Nickel Cyanide;

(5) The Determination of Benzene in Coal Gas that had been Freed from the Benzene that it originally contained and had been Mixed with Known Volumes of Benzene Vapour; and

(6) The Determination of the Vapour Tension (with reference to Benzene) of the Partially Exhausted Reagent.

(1) *The Determination of Benzene in Known Mixtures of Benzene and Air.*—Air was drawn into the gas burette and measured. It was next passed into a gas pipette containing mercury and a few cubic centimetres of liquid benzene, and was then drawn back into the burette and the increase in volume was noted. The percentage of benzene was then determined by absorption with the ammoniacal solution of nickel cyanide with the subsequent removal of the ammonia by dilute sulphuric acid in the manner described above. A large number of these analyses was made. The few results in Table IV. illustrate the average efficiency of the method.

TABLE IV.

No. of experiment	Benzene taken. Per cent.	Benzene found. Per cent.
22.	2·3	2·3
23.	2·6	2·6
24.	1·2	1·3
25.	4·9	4·9
26.	5·1	5·1
27.	2·7	2·7
28.	1·6	1·6
29.	1·8	1·8
30.	1·8	1·7
31.	5·2	5·1
32.	2·7	2·7

(2) *A Study of the Behaviour of an Ammoniacal Solution of Nickel Cyanide towards Known Mixtures of Ethylene and Air.*—Ethylene was prepared by reducing an alcoholic solution of pure ethylene bromide with a zinc-copper couple. The ethylene employed in the first experiments was made in a flask and the resulting gas was found to contain about 90 per cent of ethylene. In later experiments the preparation was carried on in a Hempel nitrometer, and the resulting ethylene was then found to be completely absorbable by 20 per cent fuming sulphuric acid. Mixtures of ethylene and air were prepared and passed over into the ammoniacal nickel cyanide. In no case was any absorption of ethylene noted after the reagent had been shaken once with the gas mixture and thus saturated with it. The data of two experiments are given as illustrative of the results here obtained: Per cent of ethylene taken 4·3, found 0·0; again, ethylene taken 10·4, found 0·0.

(To be continued).

MERCHANT VENTURERS' TECHNICAL COLLEGE.

The New Chemical Department in the Restored Building.

This department will occupy the top floor of the building, and will comprise the Chemical Lecture Theatre, the Preparation Room, the Advanced Chemical Laboratory, the Elementary Chemical Laboratory, the Balance Room, the Combustion Room, the Store Room, and the Dark Room; it will be practically isolated from the lower parts of the building, and will have a special separate ventilating and heating system.

Great care will be taken to ensure an ample supply of fresh air, and to prevent the accumulation of any fumes. The ventilation will be effected by a combination of the plenum and exhaust systems, air being driven into the rooms through heating chambers in winter and through cooling chambers in summer; it will be extracted by means of the exhaust flues placed on the benches and in the fume chambers.

The two laboratories will provide bench accommodation for sixty-six students with several auxiliary benches. Each student's place will be fitted with draught-hoods, bottle-racks, gas and water supply, and waste receptacles; the lockers, cupboards, and drawers will be so arranged that both day and evening students will have on their benches the means of locking up apparatus or materials needed for future experiments.

Three types of students' benches will be provided, one for elementary work, one for advanced work, and one suited for electro-chemical and organic work. The bench space which will be allotted to each student varies from 5 feet to 3 feet six inches.

Each laboratory will be fitted with steam-ovens and a still, also with lead-covered benches with draught-hoods suited for steam and vacuum work.

Ample fume chamber accommodation will be provided by building out from the windows on special balconies so that the whole room space may be left free. Special arrangements will be made for sulphuretted hydrogen closets in the shape of two small rooms separated from the laboratories by means of doors which will act as air locks.

Electric currents will be available, either direct or alternating, and of any desired voltage, as the department will be served directly from the machines and batteries in the electrical engineering department of the college.

The rooms and apparatus will be arranged so as to reduce the amount of moving on the part of the students to a minimum; thus the Lecture Theatre, Preparation Room, and Elementary Chemical Laboratory will form one suite, while the Balance Room, Combustion Room, and Advanced Laboratory will form another.

The Combustion Room will be fitted for blowpipe, furnace, and metallurgical work.

Although the department will be at the top of the building it will be easily reached by either of the stairways, and also by an excellent electric passenger lift.

It is impossible to give in a short space a detailed account of the fittings and apparatus, but they will include the modern details which have proved successful in recently built laboratories, as well as a considerable number of novel developments in addition to these. It is hoped that the Chemical Department will compare very favourably in every way with the most modern laboratories to be found in any of the universities or technical colleges in the United Kingdom.

PROCEEDINGS OF SOCIETIES

PHYSICAL SOCIETY.

Special General Meeting, May 22nd, 1908.

Dr. CHARLES CHREE, F.R.S., President, in the Chair.

A SPECIAL General Meeting was held to consider the proposed alterations in the Articles of Association. The principal changes were described by the Secretary, and on the motion of the CHAIRMAN, seconded by Mr. MATHER, a resolution was passed in favour of the alteration.

An Ordinary Meeting was then held.

Mr. F. P. SEXTON read a paper "*On the Spectrum Top.*"

The author explains in the paper the coloured bands which are seen when a Benham top is rotated. The best effects are obtained when the top rotates about six times per second, when the colours from the centre are purple, dull orange, yellow-green, and violet-blue for an anticlockwise rotation. When the direction of rotation is reversed the order of the colours is also reversed. The effect depends upon the position of the sector lines and on a contrast. The author assumes that the rates of growth of the colour sensations are in the order red, green, and blue where red is the greatest, and that the rates of decay are in the inverse order. Considering the inner ring with an anticlockwise rotation, the author explains the colour observed as follows:—As the black disappears the first impression will be black lines on a red ground, but this red impression will have somewhat passed to white when the sector lines disappear. Their disappearance also gives a red impression, which in this case is increased by a contrast. Finally, the disappearance of the white will give a bluish impression, not reinforced by contrast. Thus the eye will see red lines on a white ground. In the case of the second ring, the sector lines coming into view give a blue impression, depending on the amount of white preceding. When these lines pass from view they are followed by a red impression, depending on the amount of white succeeding. These two impressions combine to give a resultant orange effect. The third and outer rings are explained in a similar way.

Mr. F. E. SMITH asked if the author had viewed the top when illuminated with lights of different colours, and if so with what result.

The AUTHOR replied that experiments had not been tried in different coloured lights, as there was difficulty at the time of obtaining a coloured illumination of sufficient strength. The bands were visible in sodium light; but this did not affect the theory, because sodium light, although practically monochromatic, affects the three colour sensations.

A paper "*On the Coefficient of Diffusion*" was read by Mr. B. W. CLACK.

This paper deals with experiments which have been undertaken to test the practicability of a new method for the determination of the coefficient of diffusion of salts through water, and to find how this coefficient varies with the concentration of the solutions.

The apparatus consists of a special kind of flask of about 450 cc. capacity, fitted with a vertical glass tube of known dimensions. In the earlier experiments this was filled with distilled water and suspended by means of a fine wire in the salt solution under investigation, at the temperature of 0° C., from the arm of a chemical balance. Later, this arrangement was reversed, and the flask, filled with the salt solution, was suspended in cooled distilled water. In both methods the apparatus was so designed that one end of the vertical tube was maintained in contact with a salt solution of constant concentration, while the other end was kept in contact with distilled water. As the salt diffuses through the tube the weight of the flask varies, and an expression was deduced by which it is possible to find the value of the coefficient of diffusion from this rate of change in weight, which was automatically recorded. The accuracy in weighing was found to be greatly increased by covering the free surface of the liquid by a film of Fleuss pump-oil. As the method is complicated by the change in volume which is produced in a liquid when salt is added to it, it was found necessary to experimentally determine the value of this change in volume.

The salts experimented upon were NaCl, KCl, and KNO_3, and a large number of experiments were carried out in order to find the best relative sizes of the various parts of the apparatus and the best dimensions for the diffusion tubes.

The general conclusions may be summarised as follows:

1. The method referred to above, of filling the apparatus with the salt solution and suspending it in cooled distilled water, is much more satisfactory than the earlier method from a practical point of view. It enables greater control to be maintained over the working details, and is much simpler in operation.

2. The volume of the liquid in which the suspended apparatus is hung must be considerable. A volume of 7 litres was found to be too small, and in these experiments 13 litres was used. This was found to be sufficient.

3. With these precautions the method gives satisfactory results with a consistency of usually less than 1 per cent.

4. For a diffusion tube of 4 cm. length, no end correction need be applied, even for the widest tubes employed (1·5 cm.).

5. The coefficient for NaCl and KCl decreases as the concentration of the solution decreases.

6. For KNO_3 the opposite phenomenon is exhibited.

7. The most trustworthy results, obtained with the precautions mentioned above, for the coefficient of diffusion at 0° C., are:—

KNO_3	10 per cent	$0{\cdot}844 \times 10^{-5}$	C.G.S. unit
	5 ,,	0·870	,,
KCl	20 ,,	0·972	,,
	10 ,,	0·954	,,

Dr. A. GRIFFITHS congratulated the author upon his paper, and referred to the importance of keeping the temperature constant during the experiments. The effects of temperature changes were very marked. The importance of a deep outer vessel was also surprising, and Dr. Griffiths pointed out how it was possible to place a superior limit to the error introduced by the passage of the salt into the outer vessel. He also suggested the use of a differential method, using two glass vessels, to overcome some of the difficulties encountered in the experiments.

Prof. C. H. LEES said that all who had experience with diffusion experiments would congratulate the author. The idea of using a balance was an old one, but the author had made an old method a thoroughly reliable one. The question was still to be solved whether an increase of concentration increased or decreased the diffusion constant, and he hoped the author would be able to carry on his experiments and settle this point.

Mr. B. S. COHEN read a paper on "*The Production of Small Variable Frequency Alternating Currents suitable for Telephonic and other Measurements.*"

As an introduction a summary of the methods used by the author for such currents is given. A new method for producing these currents is then described; this consists of a form of vibrating wire interrupter which operates a make and break contact. This is used to put a source of potential on and off a resonating circuit tuned to any desired frequency. The alternating current is taken from a small transformer in the resonating circuit. A series of damped wave-trains of any frequency can be produced by this means, the trains following each other with the frequency of the wire vibrations. Several forms of circuit are described, one of which gives a train of oscillations at each break of the supply circuit. Other circuits give damped waves both on the break and on the make contact,

and by a suitable combination of two oscillating circuits worked from one mercury cup and contact it is shown that continuous and fairly uniform oscillations can be produced. The theory of action of the various circuits is briefly entered into, and the paper concludes with some applications of the waves produced to both telephonic and general electrical measurements. The wave forms given by the various circuits were shown at the meeting by means of a Duddell oscillograph.

Mr. A. CAMPBELL mentioned that with his vibrating-bar microphone hummer he had found it easy to obtain more than one frequency from the same bar by altering the supports to suitable nodal points, and tuning the magnet circuit with a condenser. Harmonics of the fundamental frequency are thus produced. He asked if any of the composite wave forms shown gave vowel sounds in the telephone.

Dr. RUSSELL congratulated the author on his interesting and valuable paper, and thanked him for the instructive demonstration he had given of methods of producing high-frequency currents suitable for telephonic and other measurements. He understood that the author's main object was not the obtaining of currents of excessively high frequency, but obtaining currents having frequencies varying between 100 and 5000 which followed the harmonic law. Some of the methods described, in particular the author's "double action circuit" method, seemed well adapted for this end. In some of these circuits there are two free periods of vibration, and it was exceedingly interesting to see the accuracy with which the oscillograph gave the resultant of two slightly damped trains of high-frequency waves of different periods. Tuning for resonance the author obtains a very perfect sine wave. He thought that the thanks of the meeting were also due to the National Telephone Company for the facilities they had afforded Mr. Cohen.

Mr. COHEN expressed his interest in Mr. Campbell's statement, that it was easy to get more than one frequency from his vibrating bar hummer. The currents shown, when passed through a telephone receiver, did not produce vowel sounds.

SOCIETY OF CHEMICAL INDUSTRY.
(LONDON SECTION).

Ordinary Meeting, June 1st, 1908.

Dr. LEWKOWITSCH in the Chair.

"*Some Modern Chemical Plant.*" By OSCAR GUTTMANN, M.Inst.C.E., F.I.C.

After discoursing on the general trend towards economy and high production per unit volume in sulphuric acid chambers, necessitated by the invention of the contact process, the author shows how greatly the yield of chambers is improved by increasing the height in proportion to the length, in fact turning the old type of chamber through 90°. Chambers are now built 48 feet square and 80 feet high, giving a capacity of about 178,000 cubic feet. The author also showed a novel method of hanging these chambers from the roof by means of vertical rods and straps.

Glover towers in Volvic lava built up in sections and held together by lead-covered iron hooks, were shown, and mention made of the feeding arrangements for Gay-Lussac towers, the best filling material for them, and the results obtained.

Next a nitric acid still holding 5 tons of nitrate of soda was described, and it was mentioned that such holding 10 tons, or fifty times as large as used twenty years ago, were already at work.

A large kiln for the manufacture of wood charcoal was of great interest, as illustrating to what extent the primitive charcoal burner's process has developed. This kiln is capable of taking 7000 cubic feet of cut wood in one charge, giving off 10,000 gallons of liquor and about 14,000,000 cubic feet of gas fuel, which latter is sufficient not only for primarily heating the kiln, but also for the whole factory.

Acid and alkali proof castings and iron-clad earthenware fans for hot acid gases were next discussed, and in conclusion the author warns against the practice of obtaining complete plans and estimates for chemical factories from engineering firms who may only make a few parts of the whole, and can have but little experience of the manufacture.

"*Explosions and the Buildings of Explosive Works.*" By OSCAR GUTTMANN, M.Inst.C.E., F.I.C.

Very little has been done in the way of modifying the construction of buildings in explosive factories since the Explosive Act of 1875, in consequence of which it became customary to make some arrangement to minimise the destructive effect of an explosion. This was attempted in various ways; the most usual being to make light wooden huts, and to surround them by earth mounds, the buildings being spaced sufficiently far apart to prevent the explosion from becoming general.

The effect of an explosion, especially with modern high power explosives, is manifested in a variety of ways, and gives rise to very curious effects.

Apart from the usual dangerous shower of heavy and burning pieces of wreckage and *débris*, the concussion, both above ground and through the ground, must be considered. The former may cause disaster by penetrating or setting fire to other buildings, while the latter manifests itself by causing the collapse and destruction of buildings by what was usually considered a suction effect. The author proposes that buildings in explosive works should be constructed in ferro-concrete with fine river gravel.

Such a structure, being practically a solid mass, would not be liable to collapse; it would be fire and lightning proof, and should an explosion take place would be so pulverised that particles could not be projected to any considerable distance.

To prevent heavy pieces of machinery and the like penetrating the roof, this is made with a double ferro-concrete skin, a layer of sand about a foot thick being interposed, which latter effectually deadens and distributes the shock. By the use of wire glass the dangerous splintering of ordinary window-panes is avoided.

The whole structure being kept relatively low, and the skin of the mounds enclosing it being also in ferro-concrete, there is a large economy effected in the amount of material and space required.

This method of construction having been favourably considered by authorities and experts, the author has thought it his duty to bring it at once before the public.

The paper was illustrated by diagrams and a large number of lantern slides illustrating the effect of explosions on surrounding buildings.

"*The Autolysator; an Apparatus foy the Automatic Estimation of Carbon Dioxide.*" By CHARLES A. KEANE, M.Sc., Ph.D., and HARRY BURROWS, A.R.C.S., Ph.D.

The "Autolysator" is an apparatus devised by Strache, Johoda, and Genzkin for the automatic estimation of carbon dioxide in furnace gases, producer gas, and similar products. It differs from other forms of apparatus for automatic analysis in giving a continuous instead of an intermittent record of the carbon dioxide content of the gases examined.

Results obtained on the laboratory scale with a gas furnace showed that the records of the instrument agree with those obtained by the ordinary analytical methods within 0·3 per cent, and that it responds very efficiently to changes in the percentages of carbon dioxide present in the gas. Experiments were also conducted on the furnace gases from boilers, and the conditions of working examined, more especially in regard to the methods of withdrawing the sample and the life of the absorbent employed.

"*The Estimation of Orcinol in Orchella Weed.*" By HENRY EDGAR WATT, M.Sc., A.I.C. (Assistant Chemist, Scientific and Technical Department, Imperial Institute).

In this paper the author shows that the published processes for the estimation of colour-yielding substance in lichens of the genus *Roccella* are open to criticism, and proposes a modified method based upon the reaction which takes place between orcinol, $CH_3.C_6H_3.(OH)_2.1.3.5$, and a solution of sodium hypochlorite. Four samples of orchella weed, received at the Imperial Institute from the Seychelles, were assayed, and particulars of the results obtained recorded.

NOTICES OF BOOKS.

Thermodynamics of Technical Gas-Reactions. By Dr. F. Haber. Translated by Arthur B. Lamb, Ph.D. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1908.

This book is a translation of a course of seven lectures delivered at the Technische Hochschule, Carlsruhe, in February, 1905, dealing with the latent heat of chemical reaction and its relation to reaction energy. After deducing the general relationships the lecturer proceeded to apply them first to the case of reactions, in which there is no change in the total number of molecules, and then to those in which the number of molecules is altered during the reaction. A very interesting chapter deals with the determination of the specific heats of gases both by direct and indirect methods, and finally the investigation of gaseous equilibria, especially at high temperatures, is discussed. The lectures dealt with a branch of thermodynamics which has not been adequately treated in any similar book, and introduced questions of great interest and technical importance, and the English translation can be recommended to chemists, both to those who are engaged in prosecuting research in technical physical chemistry and those who are teaching the elements of the same subject.

The Metallurgy of Iron. By Thomas Turner. Third Edition. London: Charles Griffin and Company, Limited. 1908.

The third edition of this work contains a new chapter dealing with the gaseous products of the blast-furnace, in which the application of the surplus furnace gases for driving gas-engines is described, and an account is given of the recovery of tar and ammonia from blast-furnace gases. In addition the important recent advances in pyrometry and in the use of the microscope are treated fully, and valuable microphotographs illustrate the chapter on the structure of cast-iron. Methods of handling and transporting ores have recently undergone considerable modifications, which are described in this new edition, and the development of American iron mines, which has led to such an enormously increased production of pig-iron, is discussed, the Lake Superior ores being treated in a special section.

Leather Trades Chemistry. By S. R. Trotman, M.A., F.I.C. London: Charles Griffin and Company, Limited. 1908.

The official and some of the more commonly employed non-official methods of analysing all materials used in the leather industry, including water and soaps, are described in this book. Both qualitative and quantitative processes are given, and the author's wide experience in leather chemistry enables him to offer to his readers valuable advice on the choice of analytical methods; he has, moreover, carefully collected from periodical and other literature examples of typical processes. Full tables are given, for instance, for the qualitative recognition of tannins, from Professor H. R. Procter's publications. The plates of the micro-photographs of the cuticles of different plants are excellently reproduced from the *Journal of the Society of Chemical Industry*. An outline of the classification and identification of dye-stuffs gives very clear schemes and tables, which, if they are carefully followed, should enable the chemist to detect any common dye comparatively easily. As a work of reference the book can be recommended, but there are objections to its use as a text-book for students, the chief being the order adopted; for example, the estimation of nitrogen by Kjeldahl's method, involving the use of standard solutions, precedes the chapter dealing with the preparation of such solutions.

Analysis of Mixed Paints, Colour Pigments, and Varnishes. By Clifford Dyer Holley, M.S., Ph.D., and E. F. Ladd, B.S. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1908.

With the aid of this book the chemist of ordinary education and experience will find little difficulty in performing an analysis of a mixed paint. The book opens with some notes on the general characteristics of the commoner mixed paints, in which some methods of adulteration are pointed out. The preparation of a sample and the separation of the vehicle and pigment are next considered, and the analysis of the former is then taken up. Special methods of oil analysis are treated in one chapter, and the methods of identifying the vehicle are made clear. The analysis of the pigments, grouped according to colour, by various systems is described fully, and examples to show the separation of the constituents from one another are included. One chapter on colour mixing contains hints for some exercises in colour-making, and an outline is given of the most satisfactory methods of analysing varnishes, both by chemical and physical and by practical tests.

Process Cost Accounts. By H. Stanley Garry, C.A. London: Gee and Co. 1908.

This volume of the "Accountants' Library" explains the outlines of the most satisfactory and correct methods of keeping accounts in relation to chemical industries. Problems which are more especially likely to occur in such trades are discussed, and typical results and examples are given to illustrate different kinds of Forms of Works Returns. The book will be found to provide accountants with considerable assistance in grasping how best to acquire a sufficient working knowledge of the technicalities of the more important processes, how to group various costs together, and finally how to represent statements and returns by charts and diagrams.

A Systematic Introduction to Analytical Chemistry. By A. F. Walden, M.A., and B. Lambert, M.A. Oxford: Joseph Thornton and Son. London: Simpkin, Marshall, Hamilton, Kent, and Co., Limited. 1908.

A useful course of analytical chemistry is given in this book, and as it is now being recognised that students who have been taught by the heuristic method may gain much by a careful study of qualitative analysis, a text-book on the subject in which new ideas are incorporated should have a successful future before it. The book differs from the older type of practical chemistry book in many respects. No tables are given, the authors believing that the construction of them by the student himself forms a most instructive exercise. The metals are grouped in the familiar five groups, and the general characteristics of each group are discussed, but separation tables for mixtures of simple salts are not given. The free use of different type emphasises the most important reactions of the metals treated, and will be an assistance to the student in the laboratory, while the explanations of obscure reactions, inserted in smaller print, will repay careful reading in the study. The acid radicles are classified according to their behaviour on treatment with hydrochloric acid and concentrated sulphuric acid, and also with silver nitrate and barium chloride, and are on the whole well treated;

insoluble substances are also included, and analysis by the dry method is discussed particularly fully. The ionic nomenclature and notation are adopted, and in the case of each metal its chief properties, the action of air and water upon it, and the reactions of its salts in aqueous solutions, are systematically studied.

Modern Pigments and their Vehicles. By FREDERICK MAIRE. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1908.

PAINTERS and dealers in paints and paint vehicles will be able to glean a good deal of useful information about pigments and their applications for various purposes from this little book. It gives a brightly written account of the properties and uses of some important pigments, and if the author is a trifle verbose he may be forgiven for the sake of the unconventionality of his style, which is of exactly the right nature to appeal to the special class of readers for whom he writes. The lists of pigments given are exceptionally full, and a good working acquaintance with the nature (but not the chemistry) of each substance may be acquired from the book; the only omission of importance among common pigments is that of lithopone, which is coming into extensive use for many purposes; the paranitraniline reds are, moreover, rapidly taking the place of quicksilver vermilion, which has now been so far superseded that it hardly deserves the space devoted to it. Some notes on the compounding of pigments and the making of the principal tints conclude a book which is of considerable value to the practical painter.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 19, May 11, 1908.

Thorium Oxyfluoride and Fluoride.—Ed. Chauvenet.—When thorium nitrate is precipitated with silver fluoride a gelatinous precipitate of the hydrated fluoride is obtained. It retains four molecules of water when dried to constant weight in a vacuum. When heated to 800° in a current of anhydrous hydrofluoric acid, a white oxyfluoride, $ThOF_2$, is obtained. The same compound can be prepared by decomposing in a slow current of hydrogen the fluosilicate of thorium obtained by precipitating a solution of thorium nitrate with hydrofluosilicic acid. Gaseous hydrofluoric acid reacts on the anhydrous bromide or iodide of thorium, giving the pure fluoride, ThF_4. Thus prepared the fluoride is amorphous, and is not attacked by sulphuric acid.

Compounds of Silver Selenide with the Selenides of Arsenic, Antimony, and Bismuth.—H. Pélabon.—The solidification point of liquid silver selenide is considerably lowered by the addition of a small quantity of Bi_2Se_3, Sb_2Se_3, or As_2Se_3. The fusion curve consists at first of an almost rectilinear part, starting from the fusion-point of Ag_2Se. This part is practically the same for all three selenides. For Bi_2Se_3 the straight line stops at 670°, which corresponds to the eutectic mixture, $Ag_2Se.\frac{1}{8}Bi_2Se_3$ or $Ag_2Se.\frac{1}{7}Bi_2Se_3$; the temperature of solidification then rises, reaches a maximum at 773° for the compound $3Ag_2Se.4Bi_2Se_3$, and then diminishes to 692°, the solidification-point of the second eutectic. The curve then becomes a straight line. In the case of antimony the first eutectic solidifies at 540°, the maximum temperature of solidification is 650° for the compound $3Ag_2Se.4Sb_2Se_3$, and the second eutectic solidifies at 573°. The second eutectic cannot be observed in the case of arsenic selenide. The fusion curves of silver selenide with the compounds SbSe, Sb_3Se_4, and Sb_4Se_5 have the same general form as those of the mixtures of silver selenide with the selenides of bismuth, arsenic, and antimony.

Origin of Ozone in the Atmosphere and the Causes of the Variations of the Carbon Dioxide in the Air.—H. Henriet and M. Bonyssy.—The ozone in the air is formed at the expense of the oxygen of the upper regions of the air under the influence of the ultra-violet radiations emanating from the sun. The ozone is brought down to the lower layers of the air by winds and by rain. When the weather is calm and the atmosphere is transparent the solar radiations act on the lower layers of air and increase the proportion of ozone. All the variations in the carbon dioxide below the normal values are due to the air of the upper regions. The variations in the carbon dioxide above the normal originate in local phenomena; for example, the respiration of men and animals in the streets of large towns, &c.

Properties of Metallic Thiosulphocarbamates.—Marcel Delépine.—The thiosulphocarbamates of nickel, cobalt, copper, sodium, barium, zinc, silver, lead, iron, which the author has prepared, exhibit the following general properties:—They tend to crystallise with their solvents. The salts of the alkalis and alkaline earths and of zinc are colourless, while those of copper, nickel, cobalt, and iron are coloured. The nickel, cobalt, iron, and copper salts, $[(C_4H_9)_2N.CS_2]_2Ni$, $[(C_4H_9)_2N.CS_2]_3Co$—Fe, are not ionised in organic solvents, and hence the salts behave indifferently towards ordinary reagents.

Amide Derivatives of *o*-Dibenzoylbenzene.—A. Guyot and P. Piquet.—Tetramethyldiamido-*o*-benzoylbenzylbenzene,—

$$(CH_3)_2N—C_6H_4—CO—C_6H_4—CH_2—C_6H_4—N(CH_3)_2,$$

may be prepared by the condensation of dimethylaniline with the chloride of dimethylamidobenzylbenzoic acid in presence of aluminium chloride. When reduced with sodium amalgam it yields tetramethyldiamido-*o*-benzhydrylbenzylbenzene,—

$$(CH_3)_2N—C_6H_4—CHOH—C_6H_4—CH_2—C_6H_4—N(CH_3)_2,$$

which, on treatment with zinc and hydrochloric acid, undergoes a further reduction to tetramethyldiamido-*o*-dibenzylbenzene,—

$$(CH_3)_2N—C_6H_4—CH_2—C_6H_4—CH_2—C_6H_4—N(CH_3)_2.$$

The benzhydrylbenzylbenzene undergoes anthracene condensation in contact with concentrated sulphuric acid in the cold. When the dimethylaniline in the preceding compounds is replaced by diethylaniline, diethyldimethyldiamido-*o*-benzoylbenzylbenzene is obtained:—

$$(C_2H_5)_2N—C_6H_4—CO—C_6H_4—CH_2—C_6H_4—N(CH_3)_2.$$

This undergoes the same reactions as the tetramethyl compound, yielding the corresponding diethyl derivatives.

MEETINGS FOR THE WEEK.

WEDNESDAY, 17th.—Microscopical, 8. "On Cycloloculina, a New Generic Type of the Foraminifera," by E. Heron-Allen. "Illuminating Apparatus for the Microscope," by J. W. Gordon. Exhibition of a New Lens for High-power Microscopy, by Mr. Gordon and Mr. H. Fletcher Moulton. Exhibition of Micro-slides, "The Development of the Chick," by A. Flatters.

THURSDAY, 18th.—Chemical, 8.30. "The Thermal Decomposition of Hydrocarbons—Part I., Methane, Ethane, Ethylene, and Acetylene," by W. A. Bone and H. F. Coward. "Rusting of Iron," by W. A. Tilden. "Studies on Elementary Zirconium," by E. Wedekind and S. J. Lewis. "Constituents of Canadian Hemp—Part I., Apocynin," and "A New Synthesis of Apocynin," by H. Finnemore. "Constitution of the Diazonium Perbromides," by F. D. Chattaway. "Cholestenone," by C. Doreé and J. A. Gardner. "A New Form of Potash Bulb," by A. E. Hill. "Solubility of Silver Chloride in Mercuric Nitrate Solutions," by B. H. Buttle and J. T. Hewitt.

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ON THE UTILISATION OF THE ATMOSPHERIC NITROGEN IN THE PRODUCTION OF CALCIUM CYANAMIDE, AND ITS USE IN AGRICULTURE AND CHEMISTRY.*

By Dr. ALBERT FRANK.

When Liebig, about the middle of last century, laid down the scientific basis of the natural laws of agriculture and the cultivation of plants, he showed that the essential condition for ensuring the soil against loss of plant-food, and thereby enabling it to maintain its fertility, was the supply of such *mineral* foods as the plants require for their growth. These mineral foods are continually being withdrawn from the soil, where they are by no means over-abundant in available form, by the crops. Among such foods Liebig placed phosphates and salts of potassium in the front rank, and thus founded his theory of *mineral manure*. As regards bodies like oxygen, hydrogen, carbon, and nitrogen, which are used for building up of the intrinsic organic plant substances, Liebig maintained, in opposition to the supporters of the vegetable theory, which was believed in up till then, that the requirements of vegetation were continually and adequately supplied by the atmosphere, and that the effect of the nitrogen contained in certain bodies widely known in practice as efficacious manures, such as bone-ash and guano, was of less importance than that of the other inorganic plant foods. Technical chemists adopted Liebig's suggestion with enthusiasm and success. After the discovery of the rich mineral phosphate deposits, the conversion of these into the higher phosphates by treatment with sulphuric acid was utilised with much success. The author's father, Professor A. Frank, of Charlottenburg, succeeded, after the Stassfurt deposits were discovered, in placing at the disposal of agriculturists, the world over, an inexhaustible supply of the much needed potassium salts. As a result of the successes achieved in agriculture by Liebig's *mineral* theory, observant investigators, and amongst the first of these Liebig himself, could not in the long run ignore the fact that, by the addition of bodies containing nitrogen to the mineral manures, an essential requirement of plant life was met, and, at the same time, an improvement in the financial condition of the manure trade must ensue. In consequence an immediate demand for manures containing nitrogen, most of them of organic origin—*e.g.*, bones, blood, offal, and fish guano—arose. These, however, only partially supplied requirements, while at the same time the Peruvian deposits of animal guanos were being very rapidly depleted by an ever increasing demand. It became necessary, therefore, to turn to those inorganic compounds of nitrogen which had definitely been proved by scientific research to be suitable for plant food. Of these the two most important were the salts of ammonia, especially ammonium sulphate, the manufacture of which on a large scale from the gas liquors was first carried out in England in the early sixties, and the nitrates, of which an extensive deposit in the form of sodium nitrate, was discovered on the rainless plateaus of Peru and Chili as early as 1830. Their application to agriculture, however, dates from 1860. Since ammonium salts have up till now only been profitably obtained as a by-product in the manufacture of coal-gas and coke, their production, in spite of the great increase from 10,000 tons in 1860 to about 600,000 tons last year (of which England uses up some 316,000 tons), is limited and dependent on other factors than agricultural demand.

* A Paper read before the Faraday Society, June 9, 1908.

Output of Ammonium Sulphate in England.

Year.	Total production (tons).	Average price per ton.	Total home consumption (tons).
1898	196,500	9 2 7½	65,000
1899	208,000	11 5 9¾	58,500
1900	210,000	11 2 0	65,000
1901	228,500	10 11 4	68,297
1902	229,000	11 16 3	68,700
1903	234,000	12 9 3	70,200
1904	245,000	12 3 8	71,200
1905	268,500	12 10 9	75,400
1906	289,000	12 0 9	78,000
1907	316,000	11 15 3	87,500

Note.—The amount used in agriculture may be anything between 90 to 75 per cent of the total home consumption, the balance being absorbed in arts and manufacture.

Output of Ammonium Sulphate in Germany.

Year.	Total (tons).	From coke (tons)	From gas works (tons).
1897	84,000	70,000	14,000
1898	98,000	84,000	14,000
1899	100,000	84,500	15,500
1900	106,500	88,500	18,000
1901	133,000	113,000	20,000
1902	140,000	117,000	23,000
1903	146,000	120,000	26,000
1904	182,000	152,000	30,000
1905	203,000	168,000	35,000
1906	235,000	197,000	38,000

It was these circumstances which placed sodium nitrate in the front rank of nitrogenous manures, and which caused the world's demand for these substances to rise from 935 tons in 1830 to about 1,740,000 in 1907 (see Fig. 1).

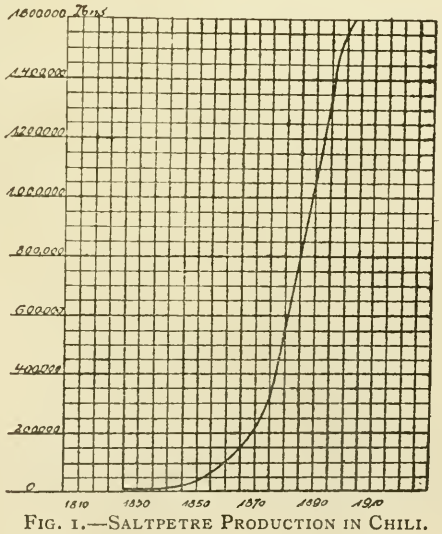

Fig. 1.—Saltpetre Production in Chili.

Of this amount Europe absorbs about 340,000 tons, 20—25 per cent of this being employed in the manufacture of chemicals and explosives, while the rest is used for agricultural purposes. Germany, which on account of the uncertain climate of its northern provinces, and because of its extensive beet-sugar industries, specially needs manures, is the largest consumer, importing over 500,000 tons yearly, about 400,000 of which are utilised in agriculture. The guano deposits which at first were considered inexhaustible

have now practically come to an end, and the same remark applies to the strictly limited nitrate deposits in the rainless region of Western South America. Agriculturists and political economists naturally regard with considerable anxiety the approaching disappearance of the deposits, while the demand for nitrates is steadily increasing year by year. Whether the date of exhaustion will be twenty or forty years hence is, on account of the vast importance of the question, of little consequence, seeing that even last year the price of sodium nitrate rose 35 to 40 per cent (in Germany), an increase due less to speculators than to higher working expenses and growing difficulty of production. It is also manifest that the chemical industries can afford to pay for the nitrate—which they consume in the production of nitrogenous compounds, nitric acid, and explosives—higher prices than the agriculturist is able to give. The price of sodium nitrate reveals, in addition, the state of the market for other nitrogenous manures. Ammonia and ammonium salts have likewise shown a marked advance, and agriculturists who have urgent need of these manures, not only for producing their present average crops, but also for securing the increased output made necessary by the growth of population, an urgent necessity pointed out some years ago by Sir William Crookes, were threatened with a serious nitrogen famine.

It is well known to all that the atmosphere surrounding our earth contains a diffused and practically inexhaustible supply of nitrogen, totalling about 4,041,200,000,000,000 tons. This works out at 31,000 tons of nitrogen over each acre of the surface of the globe, or the still air over every nine acres contains about 280,000 tons—*i.e.*, the same amount which is contained in the 1,740,000 tons of Chile saltpetre exported from that country in 1907. We know, further, that uncultivated plants, partly through certain organs which exist in them, as well as in leguminous plants, and partly by the aid of bacteria inhabiting the soil, are able to absorb the nitrogen they require from the air diffused through the soil. Furthermore, in 1775 Priestley showed that atmospheric nitrogen under the influence of the electric spark combined with atmospheric oxygen to form nitric acid, the latter being conveyed by moisture to the soil and then to the plants. But all this accumulated experimental knowledge, important though its results undoubtedly were, did not afford any clue to the possibility of producing nitrogen compounds in considerable masses, nor was it freely at the disposal of agriculturist or chemist. The method devised by Townes and Young last century, and experimentally applied by Bunsen and Playfair, showed that by passing atmospheric nitrogen over carbon and the alkalis or alkaline earths, the carbon compound cyanogen could be formed from which by further treatment ammonia could be obtained. This method, in spite of its extensive application and the many improvements which Marguerite and Sourdeval, and later Ludwig Mond, introduced in its technical details, produced no practical result, on account of the difficulty of attaining the requisite temperature. It was further complicated by the fact that the construction and maintenance of the apparatus, owing to the materials used in the furnaces, gave rise to what were then insuperable difficulties. The first successful advance was made through the discovery and application of the dynamo, which rendered it possible for electricity to be supplied in considerable quantities. By this means a hitherto unattainable temperature could be produced in quite a restricted space. Up to this time, now some few years ago, the necessary energy had to be obtained, except in so far as it was produced by reaction from the molecular energy of the elements, by means of the chemical process of "combustion." With the application of the dynamo and the invention of the electric furnace by Siemens, this process was greatly modified, as by means of electric energy thus applied heat could be produced by means of the electric arc or of an electrical resistance, and could be brought to bear directly on to the chemically reacting mixture.

With these improved means at their disposal, investigators endeavoured once more to find a solution, as already stated, of the all important question of the fixation of nitrogen.

Subsequent to 1894, when Thomas L. Willson and Moissan carried on the manufacture of carbide on a large scale in the electric furnace, the author's father, Professor Adolph Frank, in a paper published in February, 1895 ("Uber Gewinnung von Acetylen und dessen Verwendung zur Herstellung von Alkohol, &c.," *Verhandlungen des Vereins zur Beförderung des Gewerbfleisses*, No. 2, February, 1895), opposed Moissan's views as regards the possible use of this carbide combined with atmospheric nitrogen, for the preparation of cyanides and amides. Tests carried out in conjunction with Dr. N. Caro on this point established the truth of his hypotheses and further led to the invention of a method for the preparation of cyanides, cyanamides, ammonia, and other nitrogen compounds. It is on the technical and industrial manufacture of these and their value that the author has this evening to speak to you.

The other way of fixing nitrogen, on which much successful work has been accomplished, by oxidising it and turning it into nitric and nitrous acid by means of the electric spark, was soon established on practical lines, firstly with unsatisfactory technical results at Niagara Falls by Bradeley and Lovejoy, and then by the magnificent discovery of Birkeland and Eyde, as well as by the improvements which are now being perfected due to Schönbein and the Badische Anilin und Soda Fabrik. Prof. Birkeland made some highly interesting remarks on the oxidation of atmospheric nitrogen in this room in July, 1906, which you will all remember. In amplification of these the author may add that the production of calcium nitrate by the Birkeland-Eyde process seems to be developing exceedingly well in Norway, and that the factory mentioned by Prof. Birkeland is actually established at Notodden and is producing this substance. It should, however, be noticed that this industry has not made much progress in any other land save Norway, but it should not be forgotten that it is only in this northern clime that electrical energy can be as cheaply obtained on account of its unrivalled resources of water power. It would therefore seem probable that Norwegian saltpetre is destined to remain the only direct competitor of the Chilian variety.

As will be seen later on in my paper, the two methods of nitrogen fixation differ greatly as regards their chemistry. Physically they are similar; for, properly speaking, they are not electrical, but should be considered purely thermal processes. They do, however, differ in that the fixation of nitrogen by carbide is an exothermic process, in which heat is given out, while the combination of oxygen and nitrogen is endothermic—*i.e.*, it absorbs a large amount of heat, and for the fixation of an equal quantity of nitrogen requires at least three times the energy that the former process calls for.

The researches instituted, as mentioned above, by Frank and Caro in 1895 were first carried out on calcium carbide mixed with sodium carbonate. But as the yield of cyanide obtained in this way proved unsatisfactory, they soon substituted carbide of barium therefor, a substance which at that time could be more easily obtained, and this they found absorbed nitrogen isolated from the air with great avidity at a temperature of between 700° and 800° C. Frank and Caro were then contemplating the transformation of barium cyanide by treatment with carbonate of sodium or potassium into cyanide of potassium, which at that time commanded a very high price, with a considerably increasing demand. The first experimental plant was constructed with the object of perfecting as far as possible the process for obtaining cyanide of potassium and yellow prussiate. They soon found that the nitrogen absorbed by barium carbide was not merely in the form of cyanide, $Ba(CN)_2$, but that it was also present in the form of a more complex compound. The latter was found, on examination, to be cyanamide of barium, $BaCN_2$, from

which they inferred that the reaction had taken place according to the equation $BaC_2+2N=BaCN_2+C$.

Thus it appeared that in the reaction of carbide on nitrogen half of the carbon contained in the carbide had been set free. The proportion of cyanide and cyanamide of barium in the reacting mass was on an average as two to three, the product containing 30 per cent of barium cyanide and 45 per cent of barium cyanamide, the remainder consisting of barium oxide and carbon.

The transformation of the barium cyanamide into barium cyanide could be easily brought about by melting the mass containing both cyanamide and cyanide with a flux such as potash or soda, according to the equation $Ba(CN)_2+BaCN_2+C+2K_2CO_3=4KCN+2BaCO_3$. The great progress which had meanwhile been made in manufacturing carbide of calcium on an industrial scale gave rise to a renewed attempt to again try the method of treating carbide of calcium with nitrogen, which had been previously abandoned owing to the difficulties which it offered at first starting.

It was then discovered that the small yield of cyanide obtained in using carbide of calcium without an additional flux could be further reduced, and that no cyanide need be formed at all, but that the reaction would proceed in accordance with the equation $CaC_2+2N = CaCN_2+C$, and result in the formation of cyanamide of calcium alone, whilst, as has been seen, in using carbide of barium the corresponding cyanide was also formed.

About this time the patentees, Messrs. Frank and Caro, together with the well-known electrical firm Siemens and Halske, and the Deutsche Bank of Berlin, founded the Cyanid Gesellschaft of Berlin, for the further development of the process. The primary object of the new Company in taking up these inventions was to turn cyanamide of calcium into cyanide of potassium, for which there was an extensive and increasing demand for the purposes of gold extraction in South Africa and the United States. It is common knowledge that this object was successfully accomplished.

The low atomic weight of calcium carbide compared with barium carbide, owing to which 64 parts in weight of calcium carbide sufficed to bind about 28 parts of nitrogen, seemed to point to the conclusion that by using calcium carbide it might prove feasible to produce those nitrogenous compounds also in which the nitrogen would only command a low price, such as fertilisers, &c. Further research in this direction was starting with calcium cyanamide as the raw material for producing ammonia, especially when it turned out that the total nitrogen contents of the calcium cyanamide could by treatment with hot water be turned into ammonia without any difficulty or loss. The process is effected according to the equation $CaCN_2+3H_2O=CaCO_3+2(NH_3)$. In spite of the fact that this reaction requires an excess of water and a high temperature, and that acknowledged authorities on agricultural subjects passed unfavourable opinions in view of the presence of the poisonous cyanide group in the product, in consequence of a proposal made by me, an attempt was made to utilise crude calcium cyanamide directly as a fertiliser, burying it in the ground like any other manure. These experiments were first carried out in pots only. The results were satisfactory enough to indicate that the doubts entertained as to the applicability of the product as a fertiliser were groundless. Thereupon field experiments were arranged on an adequate scale at a large number of agricultural experimental stations, in most countries possessing agricultural interests, and in connection with almost every class of agricultural produce, and these have been continued for the last six years without intermission.

As has been the case with many other artificial manures, a great outcry was, and still is, made warning farmers against the use of calcium cyanamide, popularly known as nitrolim, or at least advising that it should be employed with the utmost caution. This outcry originated in the fact that not only farmers but even agriculturists are saturated with intense conservatism, and that initial failures did here and there occur when first using calcium cyanamide. It is, however, certain that manufacturers must in the first instance determine the most suitable form for every new manure, as a string of well-known instances in the case of other manures abundantly proves. Fifty years ago, when the author's father proposed the use of the potassium salts in the Stassfurt deposits, the chlorine compounds of potassium were not only considered as of doubtful value, but even as harmful, while to-day three million tons per annum are used in agriculture all the world over. In the same way there was a time when the use of Chili saltpetre was directly forbidden by the contracts of beet-sugar manufacturers, while to-day it is considered absolutely infallible by *all* agriculturists, and in certain processes quite indispensable. The storm raised against calcium cyanamide has been lulled in the same way, and recently Professor Wagner of Darmstadt, one of the greatest authorities on agricultural chemistry, summed up his exhaustive researches on the nitrogenous manuring of plants with Chili saltpetre, salts of ammonia, and calcium cyanamide as follows:—"The prospects for an advantageous use of calcium cyanamide are very bright, especially as regards its use for winter fruits. Calcium cyanamide can only be harmful in agricultural practice when it is submitted to abnormal decomposition through *unfavourable* circumstances. Such conditions are especially present in the cultivation of poor lands, such as high moorland and sandy soils which are inclined to be acid, and though rich in vegetable properties are poor in lime. It is, however, well known that this *soil behaves in an abnormal manner to other nitrogenous manures*. In order to prevent the unsuitable conditions of acid soil previous liming is necessary."

It was, besides, only natural that the manufacturers who were not in a position to turn out manure in bulk complying with all these demands should not have been very favourable. To-day, however, things are very different. A product is actually manufactured containing 20 per cent and upwards of nitrogen—that is, considerably more than did the earlier products—which recently has further been submitted to a successful dust removing process, is packed in air-tight sacks, and its efficacy appreciably increased thereby; there can be no longer any doubt that calcium cyanamide is in a position to compete industrially with any other nitrogenous manure. In this connection the question of price is of the highest importance. Now, as the cyanamide industry has been perfected in the course of the last few years, it must be considered to form, on the basis of the percentage of available nitrogen, the cheapest, and therefore for agriculturists the most economical, manure of the present time. When the first consignments of calcium cyanamide were placed on the market the question of packing and storing was not fully understood. The result was that the product absorbed a large amount of free lime, which under the influence of atmospheric moisture was naturally converted into calcium hydrate. This caused such a large increase in the volume of the material that the jute sacks containing it burst. The theoretical proportion of nitrogen showed a decrease which was not ascribed, as it should have been, to the increase in total weight, but was thought to be due to the fact that nitrolim lost nitrogen in some form or other when stored. Scientific research has shown conclusively, however, that calcium cyanamide may be kept stable for years without losing its nitrogen. The technical authorities have also taken notice of this fault, as mentioned above, and calcium cyanamide is now supplied by the manufacturers practically free from the influence of atmospheric moisture, and packed in double paper and jute sacks.

It has a further merit which is of great importance in agricultural operations where elaborate appliances are wanting: calcium cyanamide can be mixed with most widely different manures without loss. For instance, mixed manures of cyanamide and potassium salts, basic slag, &c., may be mentioned which have been found eminently successful in practice. Some difficulty is met

in mixing cyanamide with superphosphate, as the free phosphoric acid combines with the free lime of the cyanamide, and is changed from the water soluble to the citric soluble form. To a certain extent this is not preventable, but the interesting and exhaustive work of Professor Hall, the well-known agricultural chemist and director of the Rothamsted agricultural farm, on this subject has proved that, by observing certain conditions, the mixing of superphosphate with cyanamide can be easily accomplished, and is both successful and economical.

What makes cyanamide especially valuable as a manure is its after effects. It is generally decomposed by the chemical and bacteriological constituents of the soil into ammonia, which becomes fixed by the vegetable mould, and is not, as with Chili saltpetre, liable to be washed into the drains and so practically lost. For this reason cyanamide which has not been used during the *first* harvest is always available for the *second*. Researches on this subject show that the after effects of cyanamide can be very considerable according to circumstances, a property possessed by no other nitrogenous manure. As regards the economy effected by cyanamide manuring, the author will shortly describe the great number of tests which have been carried out for more than six years at agricultural research stations, and by users in all parts of the world, and render the operation of cyanamide apparent by the help of photographs.

(To be continued).

THE GRAVIMETRIC DETERMINATION OF TELLURIUM.

By VICTOR LENHER and A. W. HOMBERGER.

Of all the methods proposed for the precipitation of tellurium perhaps the one which is most used is a modification of the original method of Berzelius. He used sulphurous acid as a precipitating agent.

The method of procedure as commonly carried out consists in adding to the hydrochloric acid solution of tellurium a strong aqueous solution of sulphur dioxide, and allowing this mixture to remain in a warm place for a few days in order to effect a complete precipitation. It has been shown by Schroetter (Chemical News, lxxxvii., 17), Brauner (*Journ. Chem. Soc.*, lv., 392), Norris and Fay (*Am. Chem. Journ.*, xx., 278), Crane (*Am. Chem. Journ.*, xxiii., 408), Frerichs (*Journ. Prakt. Chem.*, lxvi., 261), and others that the precipitation by means of sulphur dioxide is far from satisfactory. Brauner has pointed out that part of the precipitated tellurium undergoes oxidation in the liquid, becoming converted into the tetrachloride, in which form it remains in solution. Crane has suggested that the main cause of the incomplete precipitation by means of sulphur dioxide is the very rapid increase in the ratio of the acids to the unprecipitated tellurium in solution, two-thirds of this being due to the hydrochloric acid set free and one-third to the sulphuric acid formed. He thought if these could be removed the reduction would be complete. The hydrochloric acid could be eliminated by evaporation, but the continuous increase in sulphuric acid would soon interrupt the reaction. This might, however, be kept under control by the addition of sodium or potassium hydroxide.

Whitehead has suggested a remedy in the use of acid sodium sulphite. He advises a moderately concentrated solution of the sulphite, and that the quantity added to the tellurium solution be sufficient only to just neutralise the acids present and that formed during the reaction. When the solution is thoroughly agitated and then allowed to stand in a warm place, the precipitate will form and settle evenly. He states that "while acid sodium sulphite does not completely remove all of the tellurium from the solution in the cold, that if not used in great excess, and the mixed solutions be raised to the boiling-point, toward the end of the action the precipitation will be perfect, and the tellurium will be obtained in a state of aggregation favourable to easy filtration."

Frerichs has worked on the basis that hydriodic acid and sulphur dioxide cause immediate and complete separation of tellurium from a tellurous solution even in the cold. and McIvor has confirmed this method (Chemical News, lxxxvii., 163).

Norris and Fay (*Am. Chem. Journ.*, xx., 278) have demonstrated that, under ordinary working conditions, precipitated tellurium increases in weight about 0·5 per cent, owing to oxidation, and that this increase is balanced by the quantity of the elements left behind as tellurium tetrachloride in the strongly acid solution in which the precipitate is formed by sulphur dioxide. They believe that it is more accurate to weigh tellurium dioxide than to weigh tellurium in the elementary state.

McIvor (Chemical News, lxxxvii., 163) and Donath (*Zeit. Angew. Chem.*, 1890, 214) have studied the precipitation of tellurium by hydrosulphurous acid. This method possesses the disadvantage of a precipitate of tellurium contaminated by more or less sulphur. The method hardly possesses any advantages over the sulphurous acid precipitation.

Stolba in 1873 (*Zeit. Anal. Chem.*, xi., 437), and later Kastner (*Zeit. Anal. Chem.*, xiii., 142). have proposed the precipitation of tellurium from an alkaline solution by means of grape-sugar.

Later, Gutbier described the precipitation of tellurium by means of hydrazine as a method for its determination (*Ber.*, xxxiv., 2724). His method of procedure is to dissolve telluric acid in warm water in a porcelain dish covered with a glass cover, and add by means of a pipette a 10 to 20 per cent solution of hydrazine hydrate. A dark blue almost black colour is noted, and after heating a short time, elementary tellurium is precipitated in a flocculent condition, the liquid becoming colourless. He continues the addition of hydrazine hydrate until the fluid is no longer coloured by further addition of the reagent.

Experimental.

Precipitation by Hydrazine.—In our hands the method of Gutbier gave fairly good results. The fact should be noted, however, that the addition of an excess of the hydrazine does not at once precipitate all of the tellurium. It is preferable to add a small amount of the precipitating agent from time to time. This necessitates several hours for complete precipitation. The following results were obtained by Gutbier's method in hydrochloric acid solution :—

TeO_2 (grm.)	0·2247	0·1988	0·2006	0·2056
Te required (grm.). ..	0·1795	0·1588	0·1603	0·1643
Te obtained (grm.) ..	0·1790	0·1577	0·1596	0·1637

Precipitation by Sodium Acid Sulphite.—In order to completely precipitate the tellurium by this reagent from a hydrochloric acid solution of a tellurous compound, the solution must contain excess of the reagent, and must be allowed to stand in a warm place for twenty-four hours. In the following experiments, the sodium acid sulphite was prepared freshly for this purpose by passing sulphur dioxide into a solution of sodium carbonate. It has been our experience that when acid sodium sulphite which has not been freshly prepared is used for the precipitation of tellurium, the precipitated element frequently contains sulphur.

That it is necessary for the solution to stand a considerable length of time is apparent from the following experiments, all of which experiments were made under exactly the same conditions. The solution of the dioxide in hydrochloric acid was brought to boiling, a saturated solution of acid sodium sulphite was added, the solution allowed to stand the requisite length of time, then brought on a Gooch platinum filter, washed with water until the filtrate no longer showed chlorides, after which it was washed with 15 cc. of alcohol, and dried at 105°.

Solution allowed to stand two hours—

Te requred (grm.)	0·1609	0·1609	0·1767	
Te obtained (grm.) ..	0·1586	0·1590	0·1744	
Error (grm.)..	−0·0023	−0·0019	−0·0023	

Allowed to stand six hours—

Te required (grm.)	0·1609	0·1609	0·1374	0·1527
Te obtained (grm.)	0·1600	0·1603	0·1366	0·1517
Error (grm.).. ..	−0·0009	−0·0006	0·0008	−0·0010

Allowed to stand twenty-four hours—

Te required (grm.)	0·1609	0·1609	0·1726	0·1286
Te obtained (grm.)	0·1615	0·1618	0·1730	0·1289
Error (grm.).. ..	+0·0006	+0·0009	+0·0004	+0·0003

After tellurium, which has been precipitated by means of sodium sulphite and hydrochloric acid, has been washed thoroughly with water and alcohol, it oxidises very slowly when heated as high as 200°, as evidenced by the following data :—

Length of time of heating.	Temperature.	Te(1).	Te(2).
15 minutes ..	105°	0·1619	0·1620
15 „ ..	105°	0·1619	0·1620
1 hour	120—130°	0·1620	0·1622
1 „	200°	0·1620	0·1623

Precipitation by means of Sulphur Dioxide.—By the treatment of tellurium dioxide dissolved in hydrochloric acid with a freshly saturated solution of sulphur dioxide, and allowing to stand for twenty-four hours, the following results were obtained :—

Te required (grm.). ..	0·1607	0·1609	0·1609	0·1609
Te obtained (grm.) ..	0·1617	0·1613	0·1615	0·1613

Unless the acidity in this precipitation is 10 per cent, the tellurium is not likely to be completely precipitated, or it will be precipitated in a very fine state of division. The solution should also be hot in order to secure satisfactory precipitation.

Simultaneous Precipitation by means of Sulphur Dioxide and Hydrazine.—By bringing both sulphur dioxide and hydrazine into a tellurium solution the whole of the element is thrown out of the solution almost instantaneously. The solution should have an acidity of 5 to 10 per cent, and it is desirable to have the solution in a high degree of concentration. The solution is brought to boiling, and 15 cc. of a saturated solution of sulphur dioxide is added, then 10 cc. of a 15 per cent solution of hydrazine hydrochloride, and again 25 cc. of the sulphur dioxide solution. The solution is boiled for a few minutes, when the elementary tellurium will settle in such a way that it can be rapidly washed. The precipitate is then transferred to a platinum Gooch filter, and washed, first, with hot water until all of the chlorine is removed, and then with 15 cc. of alcohol. The crucible and contents are then dried at 100—105°, and finally weighed.

The following results were obtained by the process as outlined above, using 10 cc. of solutions of hydrazine hydrochloride of different strengths with sulphur dioxide. Tellurium dioxide was used for the analysis :—

Strength of hydrazine hydrochloride, 20 per cent—

Te required (grm.)	0·1731	0·2065	0·1638	0·1608
Te obtained (grm.)	0·1735	0·2068	0·1641	0·1608
Error (grm.).. ..	+0·0004	+0·0003	+0·0003	—

Strength of hydrazine hydrochloride, 15 per cent—

Te required (grm.)	0·2212	0·1435	0·1605	0·1072
Te obtained (grm.)	0·2210	0·1434	0·1607	0·1070
Error (grm.).. ..	−0·0002	−0·0001	+0·0002	−0·0002

Strength of hydrazine hydrochloride, 10 per cent—

Te required (grm.)	0·1658	0·1642	0·1268	0·1422
Te obtained (grm.)	0·1656	0·1637	0·1264	0·1420
Error (grm.).. ..	−0·0002	−0·0005	−0·0004	−0·0002

That hydrazine must be there in sufficient quantity is evidenced by the following series of tests in which a 6 per cent solution was used along with sulphur dioxide, and the solution boiled only a few minutes, other conditions being exactly the same as in the preceding series of experiments.

Te required (grm.) ..	0·1508	0·1701	0·1608	0·1521	0·1903
Te obtained (grm.) ..	0·1374	0·1443	0·1535	0·1140	0·1781
Error (grm.)	−0·0134	−0·0258	−0·0073	−0·0381	−0·0122

The following two experiments were made with a large excess of sulphur dioxide water along with a 6 per cent solution of hydrazine and the solution heated six hours.

Te required (grm.)	0·1680	0·1516
Te obtained (grm.).. ..	0·1545	0·1416
Error (grm.)	−0·0135	−0·0100

The method which has been used in the laboratory of the University of Wisconsin for a number of years, and which has proven the most satisfactory for the gravimetric determination of tellurium is as follows :—The tellurium, either as derivative of the dioxide or as a tellurate, should be present in a solution which has an acidity of approximately 10 per cent of hydrochloric acid, and it is preferable to have the solution sufficiently concentrated, otherwise the fine state of division of the precipitate will render it unsatisfactory for washing. The solution is heated to boiling, and 15 cc. of a saturated solution of sulphur dioxide added, then 10 cc. of a 15 per cent solution of hydrazine hydrochloride, and, again, 25 cc. of a saturated solution of sulphur dioxide. The boiling is continued until the precipitate settles in such a way that it can be easily washed. This boiling should not take more than five minutes. The precipitated tellurium, after being allowed to settle, is washed with hot water on a Gooch filter until all of the chlorine is removed, after which the water is displaced by alcohol, and the crucible and contents dried at 105°.—*Journal of the American Chemical Society*, xxx., No. 2.

THE DETERMINATION OF BENZENE IN ILLUMINATING GAS.*

By L. M. DENNIS and ELLEN S. McCARTHY.

(Concluded from p. 284).

II. *The Absorption of Benzene by Ammoniacal Nickel Cyanide* (continued).

(3) *The Determination of Benzene in Coal-gas.*—A large number of determinations of the benzene naturally occurring in coal-gas was made by the above method and the results are given in Table V. It is perhaps unnecessary to state that here, as in all other absorption methods in gas analysis, freshly prepared reagents should first be shaken with the sample of the gas to be analysed in order to saturate the reagent with the slightly soluble constituents of the gas mixture. Moreover, the same sample of reagent should not be used for the analysis of gas mixtures of markedly different compositions.

The results given in Table V. demonstrate that an ammoniacal solution of nickel cyanide completely removes the benzene from coal-gas in two minutes. It should be understood that the gas mixture is repeatedly passed into and drawn out of the gas pipette during this time.

(4) *The Determination of the "Analytical Absorbing Power" of the Ammoniacal Solution of Nickel Cyanide.*—The term "analytical absorbing power" was introduced by Hempel and means one-fourth of the total volume of the gas that one cubic centimetre of the reagent is able to

* From the *Journal of the American Chemical Society*, xxx., No. 2.

TABLE V.

No. of experiment.	Date.	Time of contact with reagent.	Benzene found.
		Minutes.	Per cent.
33.	Jan. 7	4	0·8
34.	7	2	0·8
35.	7	2	0·8
		4 more	0·8
36.	Feb. 13	2	0·7
37.	13	2	0·7
38.	13	4	0·7
39.	13	2	0·7
40.	15	6	0·6
41.	15	4	0·6
42.	15	2	0·6
43.	18	2	0·8
44.	18	2	0·8
		2 more	0·8
45.	18	6	0·8
46.	19	2	0·5
47.	19	2	0·5
		2 more	0·5
48.	June 3	2	1·2
49.	3	2	1·2
50.	3	2	1·3
51.	3	2	1·2
52.	3	4	1·2
53.	3	4	1·2
54.	3	2	1·2
		2 more	1·2
		2 more	1·2

absorb (see Hempel, "Methods of Gas Analysis," Translated from 3rd German Edition by Dennis, p. 145). Theoretically, one cubic centimetre of the ammoniacal solution of nickel cyanide will absorb about 20 cc. of benzene vapour measured under ordinary conditions of temperature and pressure. This corresponds to an "analytical absorbing power" of 5 cc. of benzene vapour, and inasmuch as the gas pipette holds 200 cc. of the reagent, this volume should suffice for the absorption of 1000 cc. of benzene vapour. The compound that is formed, $Ni(CN)_2.NH_3.C_6H_6$, exhibits, according to the experiments of Hofmann, no measurable vapour tension.

To ascertain whether this theoretical "analytical absorbing power" was in accord with actual results, the reagent that had been used in Experiments 48 to 53 inclusive, was shaken with 2 cc. of liquid benzene (equivalent to about 500 cc. of benzene vapour) until this was completely absorbed. This reagent was then employed in Experiment 54 and in Experiments 68 to 72 inclusive. The completeness of the absorption obtained in each case shows conclusively that the limit of the absorbing power of the reagent had not yet been reached even when one filling of the pipette had taken up over 500 cc. of the benzene vapour. Further examination of the absorbing power demonstrated that even after a pipetteful of the reagent had absorbed 800 cc. of the benzene vapour, quantitative results could still be obtained. Since, however, the compound of benzene with the reagent separates as a precipitate, it is advisable, in order to avoid the clogging of the pipette, to filter the reagent after it has taken up fairly large amounts (from 200 to 400 cc.) of benzene vapour.

(5) *The Determination of Benzene in Known Mixtures of Coal-gas and Benzene.*—These determinations were carried out to ascertain whether benzene can be determined accurately in the presence of the other gases that are usually found in coal-gas. The sample of coal-gas was first freed from benzene by treatment with the ammoniacal nickel cyanide and then known amounts of benzene were added to it in the manner above described.

In Experiments 64 to 67 inclusive, one sample of coal-gas was employed, and to this successive portions of benzene vapour were added, and were then removed by absorption with the reagent. The fact that the volume of the gas residue remained constant throughout these analyses demonstrates that the constituents of ordinary coal-gas other than benzene (with the exception of those gases absorbed by a concentrated solution of potassium hydroxide) are not absorbed by the reagent. This conclusion is corroborated by the fact that in Experiments 57, 58, and 61, a prolongation of the contact between the gas and reagent did not cause further appreciable diminution in the volume of the gas residue.

TABLE VI.

No. of experiment.	Time of contact with reagent.	Benzene taken.	Benzene found.
	Minutes.	Per cent.	Per cent.
55.	2	1·1	1·1
56.	2	2·8	2·8
57.	4	0·8	0·7
58.	8	0·8	0·8
59.	2	4·3	4·3
60.	2	2·7	2·7
61.	12	2·7	2·8
62.	2	0·9	0·9
63.	2	0·7	0·7
64.	2	0·9	0·9
65.	2	1·1	1·1
66.	2	1·3	1·4
67.	2	1·3	1·3
68.	2	1·4	1·4
69.	2	1·2	1·2
70.	2	1·0	1·0
71.	2	2·6	2·7
72.	2	3.6	3·6

(6) *The Determination of the Vapour Tension (with reference to Benzene) of the Partially Exhausted Reagent.*—Although Hofmann states that the ammonia benzene nickel cyanide exhibits no appreciable vapour tension, it was still deemed desirable to ascertain whether the reagent, after somewhat extended use, would show a measurable benzene vapour tension. To this end a measured sample of air was brought into contact with a pipetteful of the reagent that had previously absorbed about 800 cc. of benzene vapour. The sample of air was then drawn back into the burette, was passed into a pipette containing dilute sulphuric acid, and was then drawn back into the burette and measured. The results were as follows:—

Volume air taken (cc.)	60·7	61·4	74·8	89·2	83·1	73·9
Volume air after contact with reagent (cc.)	60·7	61·3	74·8	89·3	81·1	73·9

From these experiments it appears that the benzene vapour tension of the partially exhausted reagent is so slight as to be negligible.

Dennis and O'Neill (*loc. cit.*, p. 507) determined experimentally that benzene is not taken up by the concentrated solution of potassium hydroxide that is employed in the Hempel method for the determination of carbon dioxide, and that consequently absorption of carbon dioxide may properly precede the determination of benzene. This point has been examined further by the authors of the present paper, who also have found that potassium hydroxide solution does not absorb benzene from mixtures of benzene vapour and air. The order of procedure then in the analysis of coal-gas should be that recommended by Dennis and O'Neill (*loc. cit.*, p. 511), the absorption of benzene being effected by the ammoniacal solution of nickel cyanide in place of the solution of ammoniacal nickel nitrate which they there suggested.

III. *The Morton Method for the Determination of Benzene in Illuminating Gas.*

D. A. Morton has recently described (*Journ. Am. Chem. Soc.*, 1906, xxviii., 1732) a simple method for the determination of benzene by absorption with concentrated sulphuric acid (sp. gr. 1·84), and before leaving this work it was thought advisable to examine Morton's method with

a view to ascertaining the accuracy of the results that can be obtained through its use. It is self-evident that for the determination of benzene in coal-gas, there must be employed an absorbent that does not remove ethylene. Morton states that the effect due to the absorption of ethylene by concentrated sulphuric acid is insignificant. This statement is somewhat surprising, for inasmuch as both benzene and ethylene are quantitatively absorbed by fuming sulphuric acid, it would seem reasonable to suppose that concentrated sulphuric acid would also take up ethylene, and that, although it might absorb this gas in smaller amounts than did the fuming sulphuric acid, the percentages of ethylene removed by it would yet be appreciable. Further, it was deemed possible that the apparently correct results in the separation of benzene and ethylene obtained by Morton might be ascribed to an accidental balancing of errors in the removal of the two gases in question. In looking up the literature of the subject it was found that Frankland and Thorne (*Journ. Chem. Soc.*, 1878, xxxiii., 89), in working upon "The Luminosity of Benzol" found "that ordinary sulphuric acid absorbs benzol vapour rather rapidly, and may be used for its eudiometric determination." They were, however, separating benzene from hydrogen, carbon monoxide, and methane, and no ethylene was present in the gas mixture that was employed. Butlerow and Gorjainow found that concentrated sulphuric acid will completely absorb ethylene at a temperature of from 160° to 170° (*Ber.*, 1873, vi., 196). Berthelot (*Ann. Chim. Phys.*, 1855, [3], xliii., 385) states that when ethylene is shaken with concentrated sulphuric acid, 100 grms. of the acid absorb 6·7 litres (120 volumes) of ethylene, and further, that the ethylene that escapes absorption upon passage through a Liebig bulb containing fuming sulphuric acid is afterward absorbed by shaking it with ordinary sulphuric acid. In a paper by Faraday (*Phil. Trans.*, 1825, p. 448) it is stated that when ethylene was allowed to stand for eighteen days in contact with concentrated sulphuric acid one volume of the acid absorbed 84·7 volumes of the ethylene.

Experimental.

The Absorption of Ethylene by Sulphuric Acid (sp. gr. 1·84).—Ethylene was prepared in the manner above described. A mixture of air and ethylene containing 22·5 per cent of ethylene was made and was shaken for one minute with about 150 cc. of concentrated sulphuric acid contained in a Hempel simple gas pipette. It was then drawn back into the burette and the diminution in volume noted. It was passed back again into the pipette and shaken for another minute and measured. This was repeated several times and the results are given in Table VII. It will be noted that 18 cc. of the 22·5 of ethylene present in the gas mixture was absorbed in thirty minutes, the rate of absorption diminishing as the percentage of ethylene decreased.

TABLE VII.

No. of expt.	Ethylene present in 100 cc. of gas mixture.	Ethylene absorbed.	Length of each shaking with concentrated H_2SO_4.	Total length of contact with concentrated H_2SO_4.	Total volume ethylene absorbed.
	Cc.	Cc.	Minutes.	Minutes.	Cc.
73.	22·5	2·3	1	1	2·3
74.	20·2	1·9	1	2	4·2
75.	18·3	1·3	1	3	5·5
76.	17·0	1·3	1	4	6·8
77.	15·7	1·2	1	5	8·0
78.	14·5	1·2	1	6	9·2
79.	13·3	0·8	1	7	10·0
80.	12·5	0·8	1	8	10·8
81.	11·7	1·0	1	9	11·8
82.	10·7	1·0	1	10	12·8
83.	9·7	0·8	1	11	13·6
84.	8·9	4·4	19	30	18·0

The Action of Concentrated Sulphuric Acid upon a Mixture of Air, Ethylene, and Benzene.—A mixture of air, ethylene, and benzene containing 1·5 per cent benzene and 10 per cent ethylene was prepared and was shaken with concentrated sulphuric acid in the manner that Morton describes, except that in Analyses 89 and 91 the shaking was continued for two minutes instead of only one minute. The results are given in Table VIII. It will be seen that of a total of 11·5 cc. of hydrocarbons in 100 cc. of the gas mixture, 8·2 cc. were absorbed in nine minutes. There was but 1·5 per cent of benzene present in the original mixture and yet 4·3 per cent of the hydrocarbons was absorbed in the first minute of shaking with the sulphuric acid, demonstrating that at least 2·8 per cent of ethylene was removed by the reagent. If the analyst is to regard the absorption by sulphuric acid as indicative of the per cent of benzene present, the actual error in this case would be very large. By further shaking of this mixture with the concentrated sulphuric acid from 0·3 per cent to 0·7 per cent more of the hydrocarbons was absorbed per minute.

TABLE VIII.

No. of expt.	Hydrocarbons present in 100 cc. gas mixture.	Hydrocarbons absorbed.	Length of contact with concentrated H_2SO_4.	Total length of contact with concentrated H_2SO_4.	Total volume hydrocarbons absorbed.
	Cc.	Cc.	Minutes.	Minutes.	Cc.
85.	11·5	4·3	1	1	4·3
86.	7·2	0·7	1	2	5·0
87.	6·5	0·3	1	3	5·3
88.	6·2	0·5	1	4	5·8
89.	5·7	1·4	2	6	7·2
90.	4·3	0·3	1	7	7·5
91.	4·0	0·7	2	9	8·2

The Action of Concentrated Sulphuric Acid upon Mixtures of Air with varying amounts of Ethylene and Benzene.—In this series of experiments the gas mixture was first shaken for one minute with the concentrated sulphuric acid and was then passed into a pipette containing ammoniacal nickel cyanide solution, to ascertain whether all of the benzene originally present had been absorbed by the sulphuric acid. An examination of the results in Table IX. shows that the gas absorbed by the concentrated sulphuric acid is not benzene alone, for upon comparing the figures in the third and fourth columns it will be seen that in Experiments 96 to 111, with the exception of the 100th and 102nd, the volume of gas absorbed is greater than the volume of benzene taken, in many cases considerably greater. Moreover, the absorption of the benzene by the concentrated sulphuric acid is frequently

TABLE IX.

No of expt.	Ethylene taken.	Benzene taken.	Hydrocarbons absorbed in one minute by concentrated sulphuric acid.	Hydrocarbons afterward absorbed by ammoniacal nickel cyanide solution.
	Per cent.	Per cent.	Per cent.	Per cent.
92.	0·3	10·8	9·9	1·2
93.	0·5	11·0	9·4	1·5
94.	0·7	7·2	6·9	0·3
95.	1·3	5·4	5·5	0·2
96.	1·3	2·7	3·0	0·2
97.	1·4	0·8	1·0	—
98.	2·1	2·1	2·5	—
99.	2·3	4·9	5·7	—
100.	2·3	2·3	2·1	0·2
101.	2·7	2·4	3·0	—
102.	2·8	5·6	5·2	0·4
103.	3·3	1·2	1·7	—
104.	3·7	1·7	2·4	0·5
105.	3·9	0·7	1·2	0·3
106.	4·2	0·7	1·2	0·1
107.	5·2	1·9	2·0	—
108.	5·2	0·9	1·3	—
109.	6·3	0·7	1·0	0·2
110.	12·6	2·9	3·3	—
111.	15·8	3·0	4·1	—

incomplete, as is demonstrated by the results in the last column. In some cases the measurements showed that the volume of gas absorbed by the sulphuric acid is greater than the volume of benzene added, and yet even in these cases not all of the benzene that had been added was removed by the sulphuric acid. (See, in particular, Experiments 96, 104, and 105). The results in Table IX. would further demonstrate that with so large and so irregular variations a correction factor for the absorption of ethylene as suggested by Morton would be of no value.

The Determination of Benzene in Coal-gas by means of Concentrated Sulphuric Acid.—A series of determinations (Table X.) of benzene in coal-gas was made by the Morton method. At the time when these analyses were made the coal-gas showed by the ammoniacal nickel cyanide method an average content of less than 1 per cent of benzene. The results by the Morton method are in every case much too high and furnish further proof that concentrated sulphuric acid removes other constituents than benzene.

TABLE X.

No. of experiment.	Date.	Length of contact with concentrated sulphuric acid.	Hydrocarbons absorbed.
		Minutes.	Per cent.
112.	Feb. 14	1	2·0
113.	14	1	1·9
114.	14	2	2·2
115.	14	4	2·8
116.	15	1	1·7
117.	15	1	1·9
118.	15	1	1·8
119.	15	2	2·1
120.	15	4	2·3

The Effect in the Morton Method of Varying the Speed of Shaking.—Morton directs that the gas be passed into the pipette containing the concentrated sulphuric acid and be shaken *vigorously* (twice per second) with this reagent for one minute. The experiments in Table XI. were made to ascertain whether the amount of absorption by the sulphuric acid would vary if the speed at which the pipette is shaken is varied. With acceleration of the shaking slightly higher results were obtained, but they can not be taken as conclusive upon the point at issue, because the concentrated sulphuric acid when shaken foams to so great an extent as to render it difficult to obtain correct measurements of the residual gas volume. Moreover, minute gas bubbles become suspended through the sulphuric acid and do not all of them rise to the surface of the reagent even after that has stood undisturbed for two minutes.

TABLE XI.

No. of expt.	Length of contact with reagent.	Number of shakes per second.	Hydrocarbons absorbed.
	Minutes.		Per cent.
121.	1	1	1·9
122.	1	1	1·8
123.	1	2	1·8
124.	1	2	2·0
125.	1	4	2·2
126.	1	4	2·3

To avoid the difficulty that results from the foaming of the reagent, due to shaking, the concentrated sulphuric acid was placed in a pipette of the type used for fuming sulphuric acid (see Hempel's "Gas Analysis," p. 229). In the first determination the sample of coal-gas was measured in the burette and was then passed into a pipette and drawn back and measured. In the second determination a fresh sample of the gas was taken and was passed into and drawn out from the pipette twice. In the next determination another sample was run into the pipette three times, and so on. The coal-gas used in Experiments 127 to 134 inclusive, was found to contain by the ammoniacal nickel cyanide method 0·8 per cent benzene. The sample of gas on the following day, February 19th, Experiments 135 to 141 inclusive, contained 0·5 per cent benzene.

TABLE XII.

No. of experiment.	Date	Number of times gas mixture passed into pipette.	Hydrocarbons absorbed.
			Per cent.
127.	Feb. 18	1	1·1
128.	18	2	1·2
129.	18	3	1·4
130.	18	3	1·0
131.	18	3	1·6
132.	18	4	1·5
133.	18	6	1·6
134.	18	10	2·0
135.	19	1	0·2
136.	19	2	0·4
137.	19	3	0·7
138.	19	4	1·0
139.	19	5	1·7
140.	19	8	2·0
141.	19	11	2·1

The results given in this table show wide variations in the apparent amount of benzene present and demonstrate that the method will not give accurate results even when the foaming is avoided by the use of the fuming sulphuric acid pipette.

Summary.

An ammoniacal solution of nickel cyanide prepared according to the directions given in this article will quantitatively absorb benzene from mixtures containing benzene and air and from ordinary coal-gas. It will not absorb measurable quantities of ethylene or of the other constituents of ordinary coal-gas, with the exception of those absorbable in potassium hydroxide solution.

The method proposed by Morton for absorbing benzene by means of sulphuric acid (sp. gr. 1·84) does not give constant results even when the conditions are the same, and yields widely varying results when the conditions are changed. Moreover, it absorbs both ethylene and benzene, and from mixtures containing both of these gases it does not quantitatively remove the benzene, but does remove an indeterminate amount of ethylene. Moreover, in the manipulation suggested by Morton, the reagent foams to such an extent as to make the accurate reading of the gas volumes well nigh impossible.

NOTICES OF BOOKS.

Exercises in Elementary Quantitative Analysis. By AZARIAH THOMAS LINCOLN, Ph.D., and JAMES HENRI WALTON, Jun., Ph.D. New York: The Macmillan Company. 1907.

THE methods of agricultural analysis as carried out in the laboratories of the American Experiment Stations are described in detail in this book. The first part deals with typical operations employed in pure quantitative analysis, and by working through this section the student will get a good acquaintance with general methods. Some important separations, as, for example, that of magnesium from calcium in a mixture of their carbonates, are described, and throughout references to larger or more specialised books are inserted in order that the student may extend his reading. The second part of the book describes the application of the general methods to agricultural products, including milk, feeding stuffs, fertilisers, and soils. In every case accuracy appears to have been placed before speed in deciding the choice of methods, and some conveniently rapid estimations are not included. Thus the Werner-Schmidt method of determining fat in milk is not described, although, in spite of its quickness, it is generally regarded as being capable of giving very accurate results when carefully performed. The last section gives a selection of

problems in stöchiometry, with answers; some of these are fairly complicated, but illustrative examples are carefully explained, and the section will give the analyst plenty of practice in working out the results of his determinations.

The Life and Work of George William Stow. By Robert B. Young, M.A., B.Sc., F.R.S.E., F.G.S. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. Cape Town: Darter Bros. and Co. 1908.

The geological and ethnological work of George William Stow in South Africa was of such importance that a biographical account of his work will be received with great interest. Not very much has been written of the spread of scientific investigation in the colony during the period in which Stow lived, which makes the little book all the more welcome, and as a record of enthusiastic pioneering work against great odds the description of Stow's labours would be hard to beat. His survey of the geology of South Africa, culminating from an industrial point of view in the discovery of the Vereeniging coalfield, and especially his "Notes on the Geology of Griqualand West," which were never published, show that he was entitled to rank high as a geologist, while his papers on the native races of South Africa were equally valuable as a contribution to ethnology.

Official Chemical Appointments. By Richard B. Pilcher, Second Edition. London: The Institute of Chemistry of Great Britain and Ireland. 1908.

The second edition of this useful reference book contains lists of the chief appointments held by chemists, including professors and teachers of chemistry, in Great Britain and Ireland, and also in India, Canada, Australia, &c. Particular care has been taken in the compilation to ensure accuracy and completeness, and in some cases notes are added upon the regulations and conditions governing the selection of candidates for important posts. A short abstract is given of certain Acts of Parliament bearing upon the chemical industries, such as the Alkali, &c., Works Regulation Act, 1906, and the duties of the officials appointed are described in outline. In addition the book contains a list of societies and institutions directly interested in the advancement of chemical science, together with some information as to their chief objects and the conditions of membership.

The Journal of the Board of Agriculture. Volume XV., No. 1, April, 1908. London: The Board of Agriculture and Fisheries.

The first number of the fifteenth volume of the *Journal of the Board of Agriculture*, published in April, exhibits many new features, which add very materially to its value for the agriculturist. The size of the journal has been considerably increased, and thus room has been made for the insertion every month of a review of the market prices of agricultural products during the preceding month, with notes on the tabular statements which have hitherto been printed at the end of each number without comment. The state of foreign crops and markets is also discussed, the trade in those commodities which compete with home-grown produce being specially considered. A new series of articles on weeds and pests opens with a description of the appearance and poisonous properties of the meadow saffron, which is illustrated by a clear and well-drawn plate, and the April number also contains the first of a series of papers on the creation of small holdings under the Act of 1907. The conditions which have enabled the existing holdings to be worked successfully will be carefully scrutinised, and it is hoped that those who are contemplating taking up holdings will be able to obtain information which may be of practical value to them.

Milk and its Relation to the Public Health. Washington: Government Printing Office. 1908.

This Bulletin, issued by the Hygienic Laboratory, contains detailed accounts written by various experts of all aspects of the relation of the milk supply to the public health. The list of authors includes many well-known American authorities who have taken a careful critical survey of every branch of the subject. The chemistry and bacteriology of milk are treated in detail, and such practical questions as the most satisfactory methods of ensuring the purity of milk by strict attention to the cleanliness of the utensils employed, of the animal itself and the milker are fully described. The importance of sanitary water supplies for farms and the best means of guarding against pollution of springs and wells is discussed in one paper, and another is devoted to the consideration of methods and results of the examination of water supplies of dairies in the district of Columbia. The tabular statements showing the epidemics of typhoid fever, scarlet fever, and diphtheria, which have been traced to the milk supply both in America and elsewhere, give a complete review of all available data relating to milk as a carrier of infection, and the diagrams illustrate very clearly the connection between milk routes and cases of infectious disease in various outbreaks.

A Laboratory Outline for Determinations in Quantitative Chemical Analysis. By Albert F. Gilman, S.B., A.M. Easton, Pa.: The Chemical Publishing Company. 1908.

In this little book the most accurate and convenient methods of determining the commoner metals and acid radicles are described fully and clearly. The details of every experiment are given so explicitly as to leave practically no possibility of doubt or misunderstanding, and questions are inserted bearing on the practical work which will force the student to think of the reasons for what he is doing and the specific purpose of the application of each reagent he uses. Most of the methods given are gravimetric, but some volumetric determinations, when they appear preferable, are also described. The electrolytic estimation of nickel is discussed rather too shortly for the student who has not had a good deal of practice and experience in electrical work. The book is interleaved with blank schemes, which can either be used as models of the entering of results of determinations into separate note-books, or else the weights obtained can be directly inserted into the book, which will then be a complete record of the student's analytical work.

Practical Methods for the Iron and Steel Works Chemist. By J. K. Heess, Ph.C. Easton, Pa.: The Chemical Publishing Co. 1908.

Although this book professes to describe practical methods of analysing iron ores, fuels, iron, steel, blast-furnace gases, &c., the explanations of the details of manipulation are so much contracted that it does not do much more than provide information as to the quantities of sample taken and reagents used. Hence the only value of the book is as a summary for the use of those chemists who are well acquainted with the processes they mean to apply, but cannot carry in their heads all the necessary numerical data. The citation of one example will be sufficient:—The analysis of gases by the Orsat apparatus (which appears as Orstat in the text) is frequently found to require some little practice and explanation, and it seems improbable that the chemist who had never used the apparatus would find that the few lines in which it is described would help him very much. So also for the colour method of determining carbon in steels, which is explained very shortly. On the other hand, one method only, and that, of course, the best in the author's estimation,

is described for the determination of each constituent, which means that the analyst has not to waste his time reading or working through various processes; he will, however, be justified in thinking that the author deserves censure for the omission of an index.

Thermoelemente und Thermosäulen. ("Thermoelements and Thermopiles"). By Professor Dr. Franz Peters. Halle-A.-S.: Wilhelm Knapp. 1908.

It is not improbable that in the future thermoelements and thermopiles may be more generally used than at present on a technical scale as sources of electrical energy, and this monograph will be found to give a clear account of their possibilities and of the directions in which our knowledge of them and their applications particularly needs extension. The theory of thermoelectricity and thermocurrents is touched upon only cursorily, and experiments of purely theoretical interest are altogether passed over. On the other hand, the history of the discovery and perfecting of thermoelements is recounted, and the preparation of thermoelements made of two metals or alloys and also those made of other substances, such as copper sulphide or lead sulphide, is described. The union of elements to form piles and their application is next treated, the last section giving a full list with short explanations of the various uses of thermoelements, more especially as instruments for conveniently and accurately measuring high temperatures.

CORRESPONDENCE.

OFFICIAL METHODS OF ANALYSIS.

To the Editor of the Chemical News.

Sir,—It is not, I believe, generally known to analysts that the Board of Agriculture have recently drafted a set of official methods which "shall be" adopted by those holding appointments as agricultural analysts under the Fertilisers Act. May I ask the use of your columns to make this fact known, and to raise a protest against a proposal which is quite new in England and opposed to the freedom which every Englishman cherishes? It is the thin edge of the wedge for the introduction of a system which will soon affect every analyst in the country, our teaching institutions, and the development of research.

So far as I am aware, there has not yet been a single case under the Fertilisers Act where analysts have differed so as to affect the question at issue. Hence there was no necessity for official methods. So much cannot be said for the analyses which have been made by public analysts under the Sale of Food and Drugs Act. It is well known that there have been wide differences in analyses, and once the principle of official methods is recognised and adopted it is certain to be applied under the Food and Drugs Act as under the Fertilisers Act.

I am strongly opposed to a hard and fast stereotyped method of analysis being adopted, and for many reasons.

First, it is well known that in the hands of competent well trained analysts the differences in results due to methods are insignificant. If they have been well trained and had experience they will know that methods in their hands can be relied upon to give concordant and accurate results. But no official method can take the place of, or do away with, the necessity for a thorough training and proper experience. It may help to turn out automatons, or analytical machines, but not analysts.

Secondly, I am opposed to them as they will hamper the educational work and chemical training which is being carried out in the country. Students will want to study only those methods. How can you expect students to take an interest, or endeavour to obtain proficiency in other methods which are not recognised, and which, when they go into laboratories as assistants, they will not be allowed to use? It will be useless for the teachers to argue that it is a good training. Unless students feel that the work they are doing will subsequently be utilised they take no interest in it.

Lastly, official methods are detrimental to all progress. What is the use of an analyst striving to perfect an old method or seeking after a new method when he knows that it cannot be adopted? Those who are acquainted with the conservatism and red tapeism of all Government departments know that it would be almost impossible to get these "official" methods changed. And for one reason, if for no other, a new method would have but little chance of adoption because, owing to the stress of work under official methods, the new method would not get the attention and trial which would enable it to be recognised as worthy of becoming official. In fact, such a body as the Society of Public Analysts, &c., might as well dissolve.

It may be argued, in opposition to my views, that official methods of analysis are in vogue both in Germany and the United States. That may be so, but I do not think that either country is very enamoured of them. Moreover, they differ essentially from those proposed by the Board of Agriculture. These latter are confined to one single method for each determination, with most minute details specified, such as add 20 cc. "drop by drop," and maintain at 70° C. "for fifteen minutes." But abroad "alternative" methods are recognised where such methods are known to give accurate results, so that the analyst has some latitude. But these so-called official methods abroad have grown up by degrees at the suggestion and by the wish of the profession to meet special requirements, and they have been and are annually discussed in public, so that all affected, as well as analysts, may be heard concerning their value and possible effects. Such a condition is very different to the publication and legalising of a series of methods by a Government department such as is now proposed by the Board of Agriculture.

The Fertilisers Act undoubtedly says the Board of Agriculture may make regulations as to the manner in which analyses are to be made. Presumably Parliament gave them this power thinking the Board would only exercise it if desirable.

I venture to think, Sir, that it is not desirable, and I trust that my brother analysts and those who are interested in the education of analysts, and in the future of chemical science, will help me to protest against the Board's unwise and unnecessary procedure.—I am, &c.,

Fredk. J. Lloyd,
Official Agricultural Analyst.

Muscovy House, E.C., June 9, 1908.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 20, May 18, 1908.

Time taken by Substances to Dissolve.—Gaston Gaillard.—As the quantity of solute increases the ratio of the time to the concentration is at first practically constant. In certain cases when the temperature is altered the curve of the reciprocal of the times resembles that of the solubility. Salts having similar coefficients may take very different times to dissolve, and the variation of the time with the temperature does not always follow that of the solubility.

Iodomercurates of Thorium and Aluminium.—A. Duboin.—The author prepared thorium iodide by decomposing thorium carbonate with hydriodic acid, and evaporating to dryness on the water-bath. Then the residue and mercuric iodide were dissolved together in water at a gentle heat. The liquid on cooling deposited, first, mercuric iodide, and then a crystalline mass which

consisted of the iodomercurate, $ThI_4.5HgI_2.18H_2O$. This salt is very easily decomposed by water. A saturated solution of mercuric iodide in a solution of aluminium iodide yields an oxyiodide in dry air. From the mother-liquor, when it is kept in a perfectly dry atmosphere, long deliquescent crystals are deposited. Analysis shows that they have the formula $AlI_3.HgI_2.8H_2O$.

Definite Compounds of Silicon and Palladium.—Paul Lebeau and Pierre Jolibois.—Silicon and palladium combine directly with evolution of enough heat to fuse the mass when they are heated together in a porcelain crucible. By this method it is possible to obtain two compounds of silicon and palladium, corresponding to the formulæ $SiPd_2$ and $SiPd$. Only the former of these has been isolated and analysed, but the existence of both compounds is proved by the perfect agreement observed in the metallographic examination and in the determination of the fusibility curve of the system silicon-palladium. The formulæ of these silicides are comparable with those of the silicides of platinum. The study of the cooling of the silicides of palladium containing less than 20 per cent of silicon has revealed a phenomenon of recalescence which seems to correspond to the crystallisation of a super-saturated solution.

Volumetric Method of Determining Tartaric Acid.—Em. Pozzi-Escot.—The raw material (tartar) is treated with a boiling solution of sodium or potassium carbonate. An integral part of the solution is acidified with hydrochloric acid, the carbon dioxide is boiled off, and ammonia is added till the liquid is alkaline. Then the tartaric acid is precipitated as barium tartrate by the addition of a known volume of a standard solution in barium bromide in alcohol. The excess of barium bromide in the filtered liquid is then determined by adding ammonium oxalate, barium oxalate being thus precipitated. It is decomposed by sulphuric acid, and the oxalic acid is estimated by titration with standard potassium permanganate.

Propargylcarbinol.—MM. Lespieau and Pariselle.—The ether, $CH_2Br—CHBr—CH_2—CH_2OCH_3$, when subjected to the action of hydrobromic acid, gives a colourless liquid tribromo-butane . 1 . 2 . 4, $CH_2Br—CHBr—CH_2—CH_2Br$. This tribromide yields with potash an ethylenic dibromide, $CH_2=CBr—CH_2—CH_2Br$, from which the corresponding alcohol, $CH_2=CBr—CH_2—CHOH$, can be prepared by the action of potassium acetate. This alcohol is attacked by an aqueous solution of potash, the product being butinol, $CH\equiv C—CH_2—CH_2OH$. Triiodobutenol is obtained by precipitating butinol with ammoniacal cuprous chloride, adding a solution of iodine in potassium iodide, and heating to 100°. The formula of the triiodide is $CI_2=CI—CH_2—CH_2OH$.

Constitution of Compounds of Tetramethyldiaminobenzhydrol with some Methylenic Derivatives.—R. Fosse.—This alcohol unites equimolecularly with β-ketonic ethers, β-diketones, and ethyl malonate, yielding one molecule of water and a series of substances which might be formed by the elimination of one molecule of water from two hydroxyl groups, thus:—

$$[(CH_3)_2N.C_6H_4]_2CH—\overset{\cdots\cdots\cdots}{:OH} + \overset{\cdots\cdots\cdots}{H:}—O—\overset{CH_3}{\overset{|}{C}}=CH—CO_2.C_2H_5$$

$$= H_2O + [(CH_3)_2N.C_6H_4]_2CH—O—\overset{CH_3}{\overset{|}{C}}=CH—CO_2.C_2H_5.$$

The author, however, has found that the compounds formed in a neutral or alkaline medium do not contain the separate oxygen atom, but the group CO. Thus the formula of the ethyl acetyl acetate is $[(CH_3)_2N.C_6H_4]_2CH—CH<\begin{matrix}CO.CH_3\\CO_2.C_2H_5\end{matrix}$.

Mixed Trihaloid Derivatives of Methane.—V. Auger.—The author has prepared the hitherto unknown compounds chloroiodoform, HCI_2Cl; bromoiodoform, HCI_2Br; and iodobromoform, $HCIBr_2$. The first of these is formed when the raw product of the action of mercuric chloride on iodoform is distilled *in vacuo*, while the fractional distillation of a mixture of equal parts of mercuric bromide and iodoform yields iodobromoform as the first of the fractions, and in the final fractions bromoiodoform is found.

Orthobenzylated Dyes from Triphenylmethane.—A. Guyot and P. Pignet.—Ortho-substituting groups exercise a protective action on dyes of the type of malachite green making them exhibit a resistance towards alkalis which varies with the nature of the group, but is independent of its positive or negative character. It is supposed that these substituents impart a special stability to the quinonic complex to which the colouration is due. If this is the case, substituting radicles with high molecular weights should exercise a pronounced influence. To verify this the authors have prepared the tetra-alcoholated-diamido-*o*-benzoylbenzyl benzene, and benzhydrylbenzyl benzene, $C_6H_4<\begin{matrix}CO\ —C_6H_4—NR_2\\CH_2—C_6H_4—NR_2\end{matrix}$ and $C_6H_4<\begin{matrix}CHOH—C_6H_4—NR_2\\CH_2\ \ —C_6H_4—NR_2\end{matrix}$. They condense easily with amines, giving orthobenzylated malachite greens or their leuco-derivatives. The dyes thus prepared are remarkably stable towards alkalis, and the protective action of the orthobenzylated group seems to be of the same order of magnitude as that of the ortho-sulphonated group.

No. 21, May 25, 1908.

Oxidation Phenomena produced by Iodic and Bromic Acids.—H. Baubigny.—Silver bromide in ammoniacal solution is said to be oxidised at 100° by iodic acid, yielding silver iodide and ammonium bromate. The author has made a study of the action of iodic acid at different temperatures on a solution of ammonia in order to explain this reaction. He has found that a gas is evolved and ammonium iodide is formed. Apparently the iodic acid oxidises the ammonia, giving water, ammonium iodide, and nitrogen, $NH_4IO_3+2NH_3=NH_4I+3H_2O+N_2$. The ammonium iodide then acts on the silver bromide in solution, giving silver iodide which is only slightly soluble in the cold. Bromic acid acts in exactly the same way as iodic acid.

Volumetric Method of Determining Simultaneously the Carbonic Acid and other Acids in Atmospheric Air.—H. Henriet and M. Bouyssy.—The air is made to bubble through a solution of soda or potash, and the alkaline liquid is divided into two parts, One-half is titrated with acetic acid, using phenolphthalein as indicator, and the reading is multiplied by two to give the total carbon dioxide. To the other half of the solution barium chloride is added, and thus barium carbonate is precipitated by the alkaline carbonate present in the liquid. The free alkali can then be titrated with acetic acid, thus giving the total acids in the air. If R is the free alkali, *c* the carbon dioxide always present in this alkali, A the acids in the air other than carbon dioxide, C the atmospheric carbon dioxide, *n* the reading corresponding to the first method of determination, and *n'* the reading of the solution into which the air has bubbled, *p* the reading corresponding to the second method of determination with barium chloride, *p'* the reading of the carbonated solution, then in the first case $R+\frac{c}{2}=n$, $R+\frac{c}{2}-A-\frac{C}{2}=n'$. In the second case $R=p$, $R-A-C=p'$. Hence—

$$A=2(n-n')-(p-p')$$
$$C=2[(p-p')-(n-n')].$$

Determination of Tungstic Acid and its Separation from other Substances by a Mixture of Chlorine and Sulphur Chloride.—F. Bourion.—When a gaseous mixture of chlorine with a little sulphur chloride is allowed to act on compounds of tungstic acid in a porcelain or silver

boat at a temperature which is gradually raised from 180° to 500°, two volatile oxychlorides, $WOCl_4$ and WO_2Cl_2, are formed. These are received in water, and the acid liquids thus obtained, after addition of nitric acid, are evaporated to dryness. The residue is taken up with a solution of ammonium nitrate (which contains hydrochloric acid when iron is present), and the tungstic acid is separated by filtration. The weight of the residue in the porcelain boat gives the weight of the chloride of the base with which the tungstic acid is combined.

MISCELLANEOUS.

The Iron and Steel Institute.—The Autumn Meeting of the Iron and Steel Institute will be held at Middlesbrough on Monday, Tuesday, Wednesday, and Thursday, September 28th, 29th, and 30th, and October 1st, 1908. An influential Reception Committee has been formed, with the Worshipful the Mayor of Middlesbrough (Lieut.-Colonel T. G. Poole, V.D.) as Chairman, and Mr. John H. Amos (Queen's Terrace, Middlesbrough) as Hon. Secretary. The provisional programme of the meeting is as follows:—On Monday, September 28th, the members will arrive at Middlesbrough, and in the evening there will be a Conversazione and Concert by invitation of the Reception Committee, in the Town Hall, Middlesbrough. The mornings of Tuesday, Wednesday, and Thursday, September 29th, 30th, and October 1st, will be devoted to the reading and discussion of papers. On Tuesday luncheon will be provided by invitation of the Reception Committee; works will be visited in the afternoon; and in the evening there will be a special performance of light opera at the Middlesbrough Grand Opera House, by invitation of the Reception Committee. On Wednesday luncheon will be provided, and in the afternoon members will be invited to the official opening of Smith's Dry Docks on the Tees, and in the evening a banquet will be given by invitation of the Reception Committee. On Thursday, October 1st, the members will be invited to luncheon by the Cleveland Institution of Engineers, the members and ladies accompanying them afterwards proceeding to Rounton Grange, where a garden party will be given by Sir Hugh and Lady Bell. By the courtesy of the Caledonian, the Great Central, the Great Northern, the Great Western, the London and North Western, the Midland, the North Eastern, and other railway companies, return tickets to Middlesbrough at a single fare and a quarter, available from September 26th to October 2nd, will be issued from London and provincial towns on production of a voucher signed by the Secretary. The proprietors of the following hotels in and near Middlesbrough have intimated that they have accommodation available for Members of the Institute:—Middlesbrough—Corporation, Grand; Stockton-on-Tees (4 miles)—Royal, Queen's; Saltburn-by-the-Sea (13 miles)—Alexandra, Zetland; Redcar (8 miles)—Coatham; Darlington (15 miles)—King's Head, Imperial. Rooms should be booked as soon as possible, as already applications have been received by the hotels. A detailed programme will be issued when the arrangements are further advanced.

MEETINGS FOR THE WEEK.

Tuesday, 23rd.—Faraday Society, 7.45. Annual General Meeting. "Recent Developments of the Kjellin and Rochling-Rodenhauser Electric Induction Furnaces," by J. Harden. "New Applications of Electro-metallurgical Alloys," by A. Jouve.

Friday, 26th.—Physical, 3.30. (By kind invitation of Dr. R. T. Glazebrook, this meeting will be held at the National Physical Laboratory, Bushy House, Teddington). Demonstrations of work in progress in the Laboratory will be given.

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THE CHEMICAL NEWS.

Vol. XCVII., No. 2535.

REFORM OF CHEMICAL AND PHYSICAL CALCULATIONS.

By C. J. T. HANSSEN.

Under this title was, in 1897, published in English, German, and Danish editions a book which, in a preface by Dr. G. Karsten, Professor of Physics on the University of Kiel, was warmly recommended, and fairly and gently noticed by scientific authorities of various nations. The Chemical News published (in vols. lxxi. and lxxii.) extracts from the manuscript, and Dr. Phil. Prof. Wilh. Foerster, Director of the Royal Observatory in Berlin, and Chairman of the International Committee of Metric Measures and Weights, wrote to the author :—

Berlin, Nov. 25, 1895.

"My opinion is that such chemical and physical investigations as developed in your 'Reform of Calculations,' apart from the ordinary course of research and study, not only now are of high importance, but ultimately may lead to very great and eminently practical simplifications of scientific work and study, and therefore are worthy of public acknowledgment and promotion.

(Signed) W. Foerster."

The Carlsberg Foundation in Copenhagen, an institution for the advancement of science, administrated by professors of the University, granted 2700 kronen (£150) to get the three editions of the book printed; many scientific journals and magazines reviewed and recommended the "Reform," and the success of the book seemed to be sure; but the author had in his "Reform" dared to protest against the "immensely accurate and absolute correct" determinations of atomic weights decreed by the *pro temp.* reigning "great masters" of chemical science and the heretical "Reform," and its author was, in the Leipzig *Zeitschrift fur Physikalische Chemie* (vol. xxv., p. 755, April 29, 1898), punished by a total and absolute condemnation.

This severe judgment, however, is now obliterated; the chemical research of the last ten years has found the errors of the atomic weights of 1898, and we know that previous to February, 1902, pure hydrogen was unknown (Chemical News, vol. lxxxv., pp. 85 and 97), and the atomic weight of many elements now expressed in plain figures show so clearly that elements combine in plain proportions, that also the plain proportion H = 1 : O = 16 must be a necessity.

This proportion has already been found by experiment in the synthesis of water. According to this proportion do 8 grms. of O combine with 1 grm. of H, producing 9 grms. of water (H_2O).

Dumas burnt 13·179 grms.	= 13179 mgrms.	O
Which combine with 13179/8 ..	= 1647⅜ „	H
Producing..	14826⅜ „	H_2O
The experiment produced	14827 „	H_2O

(Error + 1/23723).

Dumas burnt 45·887 grms.	= 45887 mgrms.	O
Which combine with 45887/8 ..	= 5735⅞ „	H
Producing..	51622⅞ „	H_2O
The experiment produced	51623 „	H_2O

(Error + 1/412983).

Erdmann and Marchand, 37·034 grms.	= 37034 mgrms.	O
Which combine with 37034/8 ..	= 4629⅜ „	H
Producing..	41663⅜ „	H_2O
The experiment produced	41664 „	H_2O

(Error + 1/55551).

The atomic weights of pure elements, consequently, are multiples of H = 1, or of Dr. G. Hinrich's pantogen = ½H. Until this proportion is finally settled may it be convenient to arrange the table of atomic weights as follows :—

Pantogen ..	½
H	1
O	16
N	14
C	12
Ag	108
	&c.

And the still unsettled elements with their decimals.

And thus, after a period of mistakes, we have found the harmonious simplicity which every true explorer of nature is searching for and hopes to find.

Upon this plain and solid foundation, and upon a few universally acknowledged laws of nature, has the author built his "Reform," and hopes that it may help to ease and simplify chemical and physical study and work, and the rational application of science to practical and useful purposes.

The author has found that at 41° 10′ geographic latitude, sea-level, mean atmosphere pressure, and the temperature of freezing water (± 0° C. = 273° C. absolute), 1 cubic metre oxygen weighs 1·428571428 5 kg. = exactly 10/7 kg., and from this determined the figures given in the accompanying table.

1 cubic metre gas.		Kgrm.		Kgrm.		Cubic metre.
Hydrogen	H	10/7 × 16	= 10/112 =	5/56 and 1 kgrm. gas	56/5	= 11·200
Oxygen	O	10/7	= 80/56 „	„	56/80	= 0·700
Nitrogen	N	14 × 5/56	= 70/56 „	„	56/70	= 0·800
Carbon	C	12 × 5/56	= 60/56 „	„	56/60	= 0·93333

The 41° 10′ latitude the author proposes to adopt as the circle of international gravity; to reduce all chemical and physical determinations of weights to this latitude, and to establish there—on the west coast of Italy—an international observatory and laboratory, similar to that by which the astronomers of all nations reduce their observations and determinations of time to the meridian of Greenwich.

By the very plain calculations given in the book, the author has found many thousands of numbers, values, and facts, which agree more nearly with the determinations of celebrated masters than those do amongst each other. The author hopes and wishes that his work may be investigated earnestly, and impartially judged.

Copenhagen V., Valdemarsgarde 3.
May, 1908.

Triboluminescence of Inorganic Substances.—Adrien Karl.—Triboluminescence appears to be a fairly common property of solids. Pure substances are not triboluminescent. A triboluminescent system preserves its property when it is subjected to various chemical transformations. Triboluminescence appears to be a property of solid solutions of a certain dilution, and thus resembles phosphorescence; it follows the same laws as this last phenomenon.—*Comptes Rendus*, cxlvi., No. 21.

THE POTENTIAL ENERGY OF THE ELEMENTS.

By DANIEL J. RANKIN.

THE elements as known to us are the most simple forms of matter that can exist in our cosmic environment.

Matter is the phenomenon exhibited by energy when in a state of integration. The differences between any two forms of matter are determined by variations in quantity of energy.

An element is a system of energy. Under normal conditions the energy exists in two states or conditions. First, the static or intrinsic energy. This intrinsic energy is incapable of being freed, is inert, is uninfluenced by any ordinary extraneous energy whether chemical, thermal, or electric. Its intensity is so enormous as to be incalculable. The phenomena alone exhibited by radio-active bodies permit us a partial realisation of its intensity. Apart from this static or intrinsic form, energy also exists in an element in a free state. The amount of this free or potential energy permits of calculation in terms of thermal calories, and this I have done in the accompanying tables.

The intrinsic energy and the potential energy of every element are fixed values, and an element cannot exist in an uncombined state when their equilibrium is disturbed beyond definite limits.

The state of integration of an element is a function of its potential.

In thermo-chemical measurements the "heat of formation" is the value of that portion of the potential which is lost or integrated, and the resulting compound undergoes diminution or increase in volume in a fixed ratio to the loss or gain of potential. As an illustration let us consider the formation of the compound Al_2S_3.

From my table we find the potentials of the constituent elements are Al = 19463 K and S = 17120 K. These quantities of energy and heat refer to such quantities of the substances as amount to their formula weights in grms. Thus—

Al_2	= 38926
S_3	= 51360
	90286 K

That is, these quantities of the elements Al + S in a free state contain 90286 large calories of free energy or potential.

The chemical combination is attended with a loss of 1224 K (heat of formation). Therefore the potential of Al_2S_3 is 90286 K − 1224 K = 89062 K.

Now as mass or volume is simply the phenomenon exhibited by the integration of energy or change due to its loss or accretion, the loss of 1224 K of energy to the system must be evidenced in a correlated loss of mass or volume.

For most elements I have found that the ratio of loss of potential to loss of volume = 1 : 1.

The volumes of the constituent elements are—

	Cc.
Al_2 .. .. .. $\frac{54{\cdot}2}{2{\cdot}583}$	= 21·031
S_3 .. .. .. $\frac{96{\cdot}18}{2{\cdot}07}$	= 46·464
	67·495

The volume of $Al_2S_3 = \frac{150{\cdot}38}{2{\cdot}26} = 66{\cdot}540$ cc.

We find, therefore, that the ratios of potentials and ratios of volumes are equivalent—

90286 : 89062 :: 1 : 0·986
67·495 : 66·540 :: 1 : 0·986

The ratio 1 : 1 holds good generally for elements whose atomic weight is below 60, with the exception of the zinc, cadmium, mercury family, where the ratio is 1 : 0·76 nearly. In such elements as sodium, calcium, and potassium the ratio is 1 : 0·65 nearly.

The following applications of these values of potential are given as illustrations.

In calculating the reactions of energy in chemical combinations containing such gaseous elements as oxygen and chlorine it is necessary to know the density of these substances in a solid form as they exist in chemical compounds. This may be effected in the following way.

To find the density of solid oxygen, in a chemical compound, let us consider the compound Cu_2O (sp. gr. 5·85).

The potentials of the constituents are—

Cu_2	15458
O	38912
	54370 K
The potential of Cu_2 + O ..	54370
Heat of formation	−408
Potential of Cu_2O	53962 K

The volume of $Cu_2O = \frac{143{\cdot}2}{5{\cdot}85} = 24{\cdot}478$ cc.

Ratio of potentials: 54370 : 53962 :: 1 : 0·992496.

Now, in this instance, the ratios of volume and potential are equivalent, *i.e.*, 1 : 0·992496. Therefore—

0·992496 : 1 :: 24·478 : 24·663 cc.,

i.e., the sum of the volumes of Cu_2 + O = 24·663 cc., but $Cu_2 = \frac{127{\cdot}2}{8{\cdot}945} = 14{\cdot}253$, and 24·663 − 14·253 leaves 10·410 cc. for the volume of 16 grms. of O.

$$\frac{16}{10{\cdot}410} = 1{\cdot}537 \text{ grms.},$$

the weight of 1 cc. of O under the conditions of integration in a chemical compound.

By a similar method the specific gravity of solid chlorine in chemical compounds may be deduced to be 2·0045.

To calculate the *heat of formation* of $PbCl_2$ (sp. gr. = 5·322):—

From my table of potentials we find—

Pb	= 969
Cl_2	= 31202
Sum of potentials of Pb + Cl_2 ..	32171 K

Volume of $PbCl_2 = \frac{277{\cdot}8}{5{\cdot}322} = 52{\cdot}194$ cc.

The sum of volumes Pb + Cl_2:—

	Cc.
Pb .. .. = $\frac{206{\cdot}7}{11{\cdot}37}$	= 18·199
Cl_2 .. .. = $\frac{70{\cdot}9}{2{\cdot}0045}$	= 35·374
	53·573

Ratio of volumes. .. 53·573 : 52·194 :: 1 : 0·97426
Ratio of potentials .. 1 : 0·97426 :: 32171 : 31343

Potential of Pb + Cl_2	= 32171
Potential of $PbCl_2$	= 31343
Loss of potential, or heat of formation..	828 K

Potential Energy of the Elements (in Large Calories).

Cu 7729	N . .. 39622	Li .. 75521	Ti .. 12380	C . .. 39050
Ag 3622	P . .. 17894	K . .. 13503	Zr .. 6568	Ru .. 3710
Au 954	As .. 7396	Rb .. 6183	Ce .. 3028	Os .. 951
Zn 7681	Sb .. 3636	Cs .. 2616	Th .. 465	B . .. 43199
Cd 3499	Er .. 1914	Im .. 1183	V . .. 11847	Rh .. 3712
Tb 1768	Bi .. 993	A . .. 14553	Nb .. 6453	Ir . .. 951
Hg 946	S . .. 17120	He .. 133743	Pr .. 3143	Be .. 52940
Al 19463	Se .. 6930	Na .. 23210	Ta .. 1590	Pd .. 3592
Ga 7535	Te .. 3228	Ca .. 13340	Cr .. 11813	Gd .. 1744
In 3675	Fl . .. 29096	Sr . .. 6107	Mo .. 6412	Pt . .. 953
Tl 965	Cl . .. 15601	Ba .. 2487	Nd .. 3125	
Si 19057	Br .. 6913	Mg .. 24124	W .. 1629	
Ge 7465	I 3210	Sc .. 13326	U . .. 437	
Sn 3559	Ne .. 28033	Y . .. 6603	Mn .. 11304	
Pb 969	Kr .. 6854	La .. 3010	Sm .. 3149	
	X . .. 3245	Yb .. 1747	O . .. 38912	
	H . .. 522564		Fe .. 11178	
			Co .. 10643	
			Ni .. 10642	

To calculate the specific gravity of a chemical compound, having given the heat of formation.

The heat of formation of Ag_2S = 33 K, to determine its specific gravity.

Potentials of constituents—

Ag_2	= 7244 K
S	= 17120
	24364 K

Potential of Ag_2+S ..	24364
Heat of formation ..	−33
Potential of Ag_2S	24331 K

Ratio of potentials, $Ag_2+S : Ag_2S$—

24364 : 24331 : : 1 : 0·99865.

Sum of volumes of constituents—

	Cc.
Ag_2 .. .. .. $\frac{215·86}{10·575}$	= 20·412
S .. .. .. $\frac{32·06}{2·07}$	= 15·488
	35·9

1 : 0·99865 : : 35·9 : 35·851 cc., volume of Ag_2S.

$\frac{247·92}{35·851}$ = 6·915, sp. gr. Ag_2S.

ON THE UTILISATION OF THE ATMOSPHERIC NITROGEN IN THE PRODUCTION OF CALCIUM CYANAMIDE, AND ITS USE IN AGRICULTURE AND CHEMISTRY.*

By Dr. ALBERT FRANK.

(Concluded from p. 292).

As regards the part which cyanamide or nitrolim plays in the soil various theories have been propounded. It appears that when brought in contact with the ground calcium cyanamide is first decomposed through the action of the moisture and of the carbonic acid in the soil into free cyanamide and carbonate of lime according to the formula $CaCN_2—H_2O—CO_2H_2CN_2—CaCO_3$.

The free cyanamide will then, by absorbing water, probably be further decomposed into urea, $H_2CN_2+H_2O=CO\frac{NH_2}{NH_2}$.

The final product of this decomposition has been found to be ammonia, but later nitrate is produced through the nitrification of the ammonia. Special experiments have demonstrated that the process of transformation of calcium cyanamide or nitrolim is assisted by a host of microbes which are to be found in almost all cultivated soil. On this point very important and interesting investigation has been carried out quite recently by Dr. Löhnis and Sabashnikoff, of Leipzig ("Untersuchungen über Kalkstickstoff und Stickstoffkalk," von Dr. Alers Sabaschnikoff,

* A Paper read before the Faraday Society, June 9, 1908.

Berlin, 1908, Verlag von Paul Pavey), and Dr. R. Perotti, of Rome ("Dottore Renato Perotti, "Su i Bacteria della Diciandiamide," Roma Typographia Enriev Voghera, 1908).

It is, however, not only to the production of fertilisers that the scope of the new calcium cyanamide industry has been limited, for it has been also successfully extended to the production from nitrolim of a number of chemical substances to a great extent by utilising derivative forms of reaction long known to science. I am able to show you here some small samples of several of these derived products, all obtained from cyanamide of calcium. Although calcium cyanamide does not display the typical character of the cyanamides, it can, by melting with fluxes, be turned into calcium cyanide, which product can then be treated by well-known methods to yield pure cyanide of potassium or sodium. The molten mass obtained by melting nitrolim with a flux contains approximately an amount of cyanide corresponding to 25 per cent KCN, the cost of the said molten mixture, to which we have given the name of "surrogate," being much less than that of an equivalent amount of pure cyanide of potassium, and the material having been shown by the investigations of English experts to be of equal efficiency with pure cyanide of potassium for the extraction of gold and silver. It appears particularly suited to the requirements of the countries where gold and silver are mined, as it can be produced with difficulty at the mine itself where it is to be used.

The production of ammonia and ammoniacal salts from nitrogen, to which I have made reference previously, has also been further worked out and perfected on an industrial scale. You will readily understand that the ammonia obtained by heating $CaCN_2$ with water is very pure and free of empyreuma. It is therefore particularly suitable for the production of pure ammoniacal salts as well as liquid ammonia (see Fig. 2).

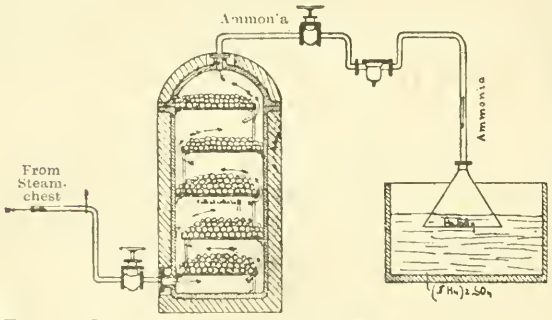


FIG. 2.—DIAGRAM OF A PLANT FOR AMMONIA PRODUCTION FROM LIME NITROGEN.

Further, the author would point out that a number of complex organic nitrogenous compounds have been derived from calcium cyanamide, and are already being produced on a manufacturing scale. Out of the great number of these I will only mention dicyandiamide, $CNNH_2$, $(—)_3$, for which there is an increasing demand in Germany for the manufacture of organic dyes, besides which there are urea, CONH, and sulphourea, $CSNH_2NH_2$.

The author would also mention that one of our German companies is producing from nitrolim the salts of guanidine, such as carbonate and nitrate of guanidine, nitro-guanidine, and other salts, all of which should now gradually come into use on an increasing scale in the industries of organic chemistry, as the cost of production will be considerably lower when starting from calcium cyanamide than by the methods of manufacture hitherto employed. Recently, attention has been paid to the use of nitrate of guanidine, nitro-guanidine, and dicyandiamide as a "deterrent" for reducing the temperature of combustion with explosives and gunpowder. In consequence of the high contents of inert nitrogen in dicyandiamide (66·6 per cent) it evolves a strong pressure when burnt in a gun, and in contradistinction to the other constituents of the explosive which contain more carbon and hydrogen, its decomposition produces but little heat. This peculiarity is of great importance in powder used with ordnance, such as cordite and filite, which, because of the high temperature of combustion, rapidly destroy the rifling of the barrels. With many powder mixtures the cooling action of dicyandiamide is shown by the disappearance of the flash at the muzzle, so that on discharge both powder-smoke and powder-flash are done away with.

The composition of the crude cyanamide of calcium made it appear likely that it would lend itself quite as well as yellow prussiate and potassium cyanide for use in case-hardening, and tempering of iron and steel. Tests carried out to this end have confirmed this impression. It has been shown that by adding certain fluxes to the crude cyanamide of calcium a very high hardening effect can be produced. This new hardening mixture, under the name "ferrodur," has been introduced on the market in Germany, England, and other countries, and its property of producing an extraordinary depth of the hardened surface without the material being at all deteriorated has already secured it a great number of friends.

If I may ask your indulgence for a few more minutes, I would like to give you a short description of the method by which the nitrolim is being produced in some of the factories, and to say also a few words on its position in the markets of the world. The carbide coming from the electric furnaces is ground, charged into retorts made of fire-proof material which are mounted in a furnace similar to gas-house furnaces (see Fig. 3). The nitrogen is then

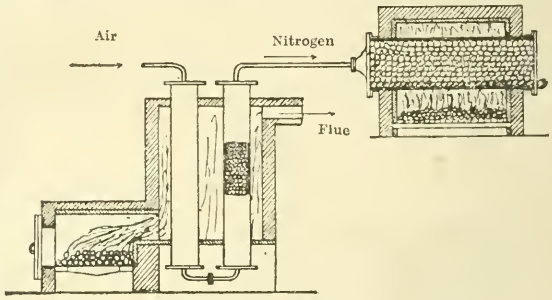


FIG. 3.—DIAGRAM OF A LIME NITROGEN PLANT.

passed over the carbide at a temperature of from 800° to 1000° C. The carbide used is of the same quality and percentage as that employed for lighting purposes, and the nitrogen consumed is obtained by fractional distillation of liquefied air by the Linde system, or the so-called "copper" process in which air has passed through heated copper particles. The copper takes up the oxygen and the free nitrogen passes to the furnaces. The resulting copper oxide is reduced in the same apparatus by treatment with reducing gases or vapours, and the copper which is recovered is then ready for a new cycle. In the Linde process the oxygen remaining after separation of the nitrogen may be utilised for any purposes. As soon as the carbide in the retorts is saturated with nitrogen, a fact which will be made apparent by the controlling gas-meter coming to a standstill, the calcium cyanamide is extracted from the retorts in the form of a hard cake, and cooled while the air is excluded. It is then ground into a fine powder, and is ready for use. During the last year a new electric furnace has been developed for treating carbide with nitrogen, and is being universally adopted by all the new cyanamide factories in preference to the older retorts. This process is cheaper to instal and to operate where the cost of power is lower than the retort furnaces just described; and notwithstanding that the average life of the retorts has been greatly prolonged, the new electric furnace is cheaper to maintain, possessing practically an unlimited life.

Crude nitrolim contains about 57 to 63 per cent of the pure cyanamide of calcium, so that its total contents in nitrogen will amount to roundly 20 to 22 per cent, the same as sulphate of ammonia. The material contains besides this about 20 per cent of calcium oxide, 7 to 8 per cent of silicious acid, iron oxide, and alumina, and 14 per cent of carbon, which imparts to the product its characteristic slate-black colour.

Most carbide works obtain at the present time a yield of two tons of carbide per kw. year, and two tons of carbide will combine with practically 500 kilogrms. of nitrogen in the form of nitrolim; a power of two kw., or 2⅔ horse-power, is required per year for fixing one ton of nitrogen by the Frank-Caro process. In addition thereto, about ⅓ horse-power is required for grinding and all other operations. If, therefore, it were proposed to substitute nitrolim for the nitrate of soda at present consumed in the world, it would require plants disposing of no less than 800,000 horse-power to do so.

It goes without saying that before the process of making nitrolim could be developed on an industrial scale, its value as a fertiliser had first to be ascertained. And as it naturally took a number of years to complete the exhaustive agricultural researches instituted for this purpose sufficiently to make them conclusive, it will not surprise you, gentlemen, that it was only about three years ago that the question of putting up industrial works was attacked.

About that time the Cyanid-Gesellschaft, in conjunction with two important Italian companies chiefly interested in the mauufacture of calcium carbide, promoted, under the management of Cav. Morani, the founder of the Italian Carbide Industry, the Societa Generale per la Cianamide in Rome.

The first plant on a large industrial scale was started about two and a-half years ago at Piano d'Orta in Central Italy (see Fig. 3), near to the Adriatic Sea, for a yearly production of 4000 tons of lime nitrogen, and is just now being enlarged to a capacity of 10,000 tons. In addition to this, the Societa Generale is also about to appropriate a large water-power it owns in Italy for the erection of other works. One is ready to start in Terni in connection with the large carbide factories there, and another factory is in course of erection in San Michel in the Val d'Aosta.

There are at present in Austria-Hungary important cyanamide works in course of erection, all promoted by the Societa Generale of Rome. In Sebenico, in Dalmatia, at the carbide works one is being built for an initial yearly production of 4000 tons. At Fiume, in Istria, works are also in construction for a similar output.

At the present time a water-power installation of at least 50,000 horse-power is being erected at Almissa, also in Dalmatia, for the manufacture of this new artificial manure. The market for the products of these works will be the Balkans, Asia Minor, and Egypt, where, owing to the practice of irrigation, nitrolim will be of special value to agriculture.

In France, the Société Francaise des Produits Azotés installed works a few months ago at Nôtre Dame de Briançon (Haute Savoie), for the manufacture of cyanamide, with an output of about 4000 tons per annum. In the Rhone Valley in Switzerland the Société Suisse des Produits Azotés has just opened equally important works. In Germany, the works at Westeregeln and Brühl on the Rhine are manufacturing 10,000 tons of nitrolim annually. It is interesting to mention that the works at Brühl for the preparation of carbide do not employ water-power, but produce the power required in the works themselves, using cheap coal in large quantities for this purpose. Another installation is that of the Brandenburgischer Carbidwerke for the preparation of nitrolim with an output of 2500 tons per annum, near Bromberg, in North Germany, which is also completed, while the large works of the Cyanid Gesellschaft for an output of over 15,000 tons of nitrolim at Alz-Fluss, in Bavaria, are at present in construction. In the United States of North America the American Cyanamide Company has taken up the manufacture of nitrolim, and are constructing on the Canadian side of the Niagara Falls works of a present capacity of from 5000 to 6000 tons per annum, to be enlarged later to an output of 40,000 tons.

It is quite natural that English enterprise should have given this new artificial fertiliser considerable attention. The North-Western Cyanamide Co., Ltd., with a capital of £120,000, was incorporated in the middle of 1906 to acquire from the Societa Generale and work licences for the manufacture and sale of cyanamide in a vast territory comprising the United Kingdom, the Colonies, Protectorates and Dependencies (excepting Canada and Egypt), and a large portion of the North-West of Europe, viz., Norway, Sweden, and Belgium, with 30 per cent of the consumption of Denmark, Germany, and Holland. The Sun Gas Company, now widely known as the Alby United Carbide Factories, Ltd., and their able Board of Directors, Mr. Albert Vickers, Sir Vincent Caillard, Mr. A. E. Barton, and others, took a leading part, with the co-operation and assistance of the Societa Generale of Rome, in the promotion of the North-Western Cyanamide Co., the Alby Company undertaking the erection of a new factory adjoining to that of the North-Western Company to supply them with the requisite carbide. These works, erected at Odda, situated at the head of the beautiful Hardanjer Fjord, you will see in the picture, which shows the carbide works and the adjoining nitrolim works, the largest at present constructed. The capacity of the cyanamide works at present is 12,500 tons of nitrolim, and is laid out so as to be eventually enlarged to 50,000 tons. The nitrogen is produced by the largest Linde pump ever erected, with a capacity of 375 cubic metres per hour, and the latest electrical furnaces are there installed. The author wishes to point out here that the works at Odda, which produce 2500 tons of nitrogen, only employ from 5000 to 6000 kw., whereas from the statement of Mr. Eyde (extract from the "Archives of the Deutschen Landwirtschaffsrats," 31rst year, 1908) it appears that in the works at Notodden, in Norway, for the preparation of an equivalent amount of nitrogen in the form of nitrate of calcium 25,000 kw. are required.

In order to complete the review which the author has made of the works already erected for the preparation of nitrogenous fertilisers, it should be stated that the British allies in the Far East, the Japanese, are erecting in the south of the Kinskzu Island a works capable of producing 4000 tons per annum, so that the manufacture of the new fertiliser will soon be localised all over the world.

At the end of the present year, works for a total production of over 45,000 tons of nitrogen will be in full swing, and in the course of next year there will be a correspondingly large increase in the means of production of this product.

Though these figures may appear relatively high, they are quite diminutive in comparison with the continual increase in the demand for nitrogenous food for our agriculture, which in Germany alone at the present time shows an annual increase of 15,000 tons of nitrogen.

It would be an error to assume that the competition of calcium cyanamide on the fertiliser market with Chili saltpetre, sulphate of ammonia, or Norwegian saltpetre can take on the character of a war of annihilation, as was the case with artificial indigo in respect to the natural product. On the contrary, Industry and Agriculture will welcome increasingly large supplies of nitrogen, tending to prevent the rising in the prices of the nitrogenous foods required for the development of plant life.

It will be an especial satisfaction to you, gentlemen, to be assured that just at the present juncture discoveries in the field of electrical chemistry have made it possible to succeed in the attempt to supply vegetation with its most valuable food, and that in the future the increasing demands for this form of nutrition by agriculturists can be satisfied, and mankind will, for the future, be able to manufacture unlimited bread and strength.

Discussion.

Mr. Henry Cottrell pointed out that a great advantage of these artificial nitrogenous manures is that they are alkaline, whereas the native nitrates are acid and produce in time sickness in the soil. It was difficult to persuade the farmer, however, to use new manures.

Mr. Walter Reid, referring to some tests he had made on calcium cyanamide, drew attention to the moisture in the soil as having considerable effect on the results of such tests. With regard to the use of calcium cyanamide in smokeless powder, he had found it rather too efficient in slowing the explosion.

Dr. H. Borns hoped the author would furnish some fuller details regarding the efficiency and construction of the electric furnaces in which combination of nitrogen with carbide took place.

Dr. J. H. Voelcker said farmers could not be expected to use new manures until they were perfectly satisfied as to their cost and effect. There were, for example, at present certain disadvantages connected with the use of nitrolim which would have to be eliminated before it could become entirely satisfactory. Beyond that, the situation was determined entirely by price.

Mr. W. Murray Morrison asked whether the cyanamide could not be made direct from limestone and coal in one operation.

Mr. J. L. F. Vogel asked what fear there was of a charge of carbide not being completely nitrated.

The Chairman (Dr. F. Mollwo Perkin) drew attention to the use of cyanamide in synthesis, and hoped that some of the very interesting and important compounds that could be made from it would be manufactured in this country.

Dr. Frank replied to the points raised by the various speakers. Cyanamide was 10 per cent cheaper than ammonium sulphate. Its stability was good; although the lime absorbed moisure, there was no loss of nitrogen. Up to the present its manufacture in one operation had not proved successful.

(For the woodcuts illustrating this article we are indebted to the courtesy of the Secretary of the Faraday Society).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 4th, 1908.

Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

Mr. J. Gibson was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Thomas Aubertin, B.A., care of Messrs. George Anderson and Co., Ltd., Carnoustie, N.B.; John William Pearson, B.A., Buxton College, Buxton; Frank Perry, 63, Tunnel Street, Coseley, near Bilston, Staffs.; George O'Brien Power, Fatehpur, U.P. of Agra and Oudh, India; William Frothingham Roach, M.D., M.S., Royal Mersey Yacht Club, Rock Ferry, Cheshire.

Of the following papers, those marked * were read:—

*124. "*The Interaction of Copper and Nitric Acid in presence of Metallic Nitrates considered with reference to the Existence of Hydrates in Solution.*" By Edward Henry Rennie, Alfred James Higgin, and William Tennant Cooke.

The authors find that in most cases the addition of metallic nitrates greatly accelerates the dissolution of copper in nitric acid, but that nitrates, such as those of rubidium and cæsium, cause considerable retardation. They consider that these effects are due to the withdrawal by the salts of water or nitric acid from the solution, and the consequent concentration or dilution of the acid, and regard their results as confirmatory of the views now generally held that combination takes place between solvent and solute. They find, moreover, that the accelerations produced by the nitrates of any one group of metals decrease as the atomic weights of the metals increase. When copper nitrate is added to the nitric acid, the dissolution is greatly accelerated. Hence the view that the auto-acceleration always observed when copper is dissolved in nitric acid is due to nitrous acid requires to be modified, the accumulation of copper nitrate in the solution being an important factor in the progress of the change.

Discussion.

Dr. Veley remarked that the results obtained by the authors might in some cases be due, not to the nitrates *per se*, but also to the nitrous acid or nitrites formed therefrom. Thus, when the conditions are such that copper dissolves in nitric acid (containing nitrous acid), copper nitrite is initially formed, which is subsequently converted into the nitrate. It appeared to him that it would be of interest if the authors were to extend their investigations to metals other than copper, such as mercury, which dissolves initially as mercurous nitrite, yielding mercurous nitrate, and, finally, mercuric nitrate under certain conditions. Silver and bismuth behave generally as copper.

Mr. W. C. Reynolds pointed out that nitric acid, with or without the presence of nitrates, has no action whatever on metallic copper if it is freed from traces of nitrous acid, even in the case of much stronger acid than that referred to. This could be effected in a few seconds at the ordinary temperature by adding a trace of sodium peroxide to the acid solution—the addition of carbamide was not so effective.

The alkaloids, morphine, and especially brucine, afford colour tests for the presence of nitrous acid in such acid solutions, and the addition of either should cause no coloration for some hours in the absence of nitrous acid (Reynolds and Sutcliffe, *Journ. Soc. Chem. Ind.*, 1906, xxv., 512). He thought some of the apparently anomalous results obtained by the authors might be due to the varying amount of the "trace" present.

Prof. Armstrong (who had given an account of the paper) said that, whilst he was in accord with the authors that salts exercised a "concentrating effect," he did not think that the acceleration observed was due to the direct withdrawal of water from the nitric acid; the acid used was too dilute and the proportion of salt too small to account, on such an assumption, for the effects produced. It was, however, well known that the dissolution of copper was dependent on the presence of nitrous compounds, and he was inclined to think that salts produced their effect by modifying the condition of these compounds in solution. From this point of view, the observations were most striking and valuable as throwing fresh light on the changes involved in the dissolution of metals in presence of nitric acid.

As to the influence of copper nitrate, it was to be remembered that the heat of dissolution of copper in nitric acid is a negative quantity, and that, from this point of view, copper nitrate is a more effective solvent of copper than the acid.

*125. "*The Triazo-group.* Part IV. *Allylazoimide.*" By Martin Onslow Forster and Hans Eduard Fierz.

Allylazoimide, $CH_2{:}CH{\cdot}CH_2{\cdot}N_3$, prepared with some difficulty from allyl chloride and sodium azide, is a mobile refractive liquid which boils at 76·5° under 760 mm. pressure; owing to subsidiary changes the yield is disappointing. The *dibromide*, $C_3H_5N_3Br_2$, is a heavy colourless liquid, boiling at 87° under 5 mm. pressure.

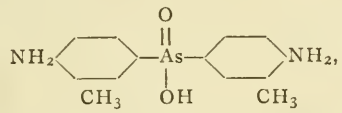
The diazoamino-*compound*, $C_3H_5N_3$, arises from allylazoimide by spontaneous isomeric change, crystallising from the liquid azoimide in colourless transparent lustrous prisms, which melt and decompose at 192°; the substance is bimolecular, and is remarkably sensitive towards dilute

acids, including acetic, which liberates two-thirds of the nitrogen in elemental form.

*126. "*Aromatic Arsonic and Arsinic Acids.*" By Frank Lee Pyman and William Colebrook Reynolds.

In the preparation of *p*-aminophenylarsonic acid and 2-aminotolyl-5-arsonic acid, the corresponding bisaminoarylarsinic acids, which have been briefly alluded to by Benda and Kahn (*Ber.*, 1908, xli., 1672), were obtained. The isolation of these by-products was described, and the following new substances were characterised :—

Bis-2-aminotolyl-5-arsinic acid,—



forms highly refracting microscopic needles, melting and decomposing at 247—249°. The *sodium* salt forms large, hard, prismatic needles, which melt at 74—75°, and contain 7½ molecular proportions of water of crystallisation.

Bis-2-acetylaminotolyl-5-arsinic acid,—

$$C_{18}H_{21}O_4N_2As,\tfrac{3}{2}H_2O,$$

crystallises from water in highly refracting microscopic prisms, melting at 242—244°.

Its *sodium* salt forms radial clusters of silky needles, which melt at 106—107°, and contain 6 molecules of water of crystallisation.

Bis-p-aminophenylarsinic acid, $C_{12}H_{13}O_2N_2As$, forms matted needles melting at 248—249°. Its *sodium* salt crystallises in large monoclinic plates, containing between 5 and 6 molecular proportions of water of crystallisation; its *barium* salt forms large hard prisms containing 7½ molecular proportions of water of crystallisation.

Bis-p-acetylaminophenylarsinic acid,—

$$C_{16}H_{17}O_4N_2As,3H_2O,$$

crystallises from water in rosettes of needles, and melts at 275°. Its *sodium* salt forms prismatic needles containing 9 molecules of water of crystallisation.

Discussion.

The President inquired whether, in view of the fact that antimony compounds appeared to be more effective than arsenic compounds as a remedy for sleeping sickness, any attempts had been successful to form similar compounds with antimonic acid ?

Dr. Pyman replied that no such attempts had as yet proved successful.

127. "*Condensation Products from Aminopinenedicarboxylic Acid.*" By William Godden.

Condensation products of glycine and aspartic acid with aminopinenedicarboxylic acid have been obtained, and their copper salts prepared.

128. "*A Delicate Test for Bromides alone or in Solution with Chlorides.*" By James Sprunt Jamieson.

The solution to be tested is heated to boiling with 1 or 2 cc. of dilute sulphuric acid and 1 or 2 cc. of potassium dichromate ; it is then cooled, and shaken with chloroform. The chloroform layer is separated, washed two or three times with water, and finally shaken with a little dilute potassium iodide solution. In the presence of a bromide, the chloroform is coloured violet, due to the liberated iodine.

The following equation probably represents the reaction :

$$6NaBr + K_2Cr_2O_7 + 7H_2SO_4 = 3Na_2SO_4 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3Br_2.$$

The above reaction will detect 0·5 mgrm. of sodium or potassium bromide, either free or in presence of sodium chloride.

129. "*Experiments on the Synthesis of* 1-*Methyl*cyclo*hexylidene*-4-*acetic Acid*, $CHMe<^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}>C{:}CH\cdot CO_2H$." (Part I.). By William Henry Perkin, jun., and William Jackson Pope.

The authors have continued the work of which a preliminary account has already appeared (*Proc.*, 1906, xxii., 107).

130. "*A Method for the Measurement of Rate of Change in Solid Alloys.*" (Preliminary Note). By Guy Dunstan Bengough.

The method consists in heating portions of the metastable alloy at a selected temperature for various lengths of time. The portions are then quenched in water to stereotype as far as possible the phases present at the selected temperature. Photomicrographs are made at a magnification determined by the coarseness of the crystalline structure. From the entire negative, an enlargement is made on bromide paper, the degree of enlargement again depending on the coarseness of the structure. The relative proportions of the phases present may then be determined by cutting them out separately, and weighing. Curves are then plotted with axes representing time and percentages of any given constituent, showing the rate of change at the selected temperature.

Tests made on the uniformity of the bromide paper used for the enlargement and on the difference in weight between portions of the paper which printed black and white respectively have shown that the errors due to these causes are negligibly small when compared with some others inherent in the process.

Duplicate measurements of the percentage of one of the constituents in a copper-zinc alloy gave the following results :—

	Proportion of *a*-constituent.		Mean.
	i.	ii.	
Alloy—Cu, 60 per cent ; Zn, 40 per cent	67·3	67·7	67·5
Another specimen of the same alloy	67·5	67·7	67·6
Another specimen annealed 7 hours at 540° and slowly cooled ..	89·2	89·3	89·25

By careful selection of typical portions of the alloy, and with crystalline structures suitable to the method, the limit of accuracy appears to be about ± 0·25 per cent.

Comparative tests have been made to ascertain how far planimetric measurements of the areas of the phases after enlargement agree with the results obtained by the method described :—

	Proportion of *a*-constituent.			
	By planimeter.		By weighing.	
Alloy—Cu, 60 per cent ; Zn, 40 per cent	59·2	58·5	59·6	60·0
Mean	58·85		59·8	
Same, annealed at 640° and slowly cooled ..	64·6	64·2	65·3	64·6
Mean	64·4		64·95	

The planimeter gives the lower result in both cases, for a reason not yet ascertained. The actual proportions of the *a*-constituent in the above experiments have no significance; they depend on the rate of cooling adopted in the various experiments. The particular alloys used have merely been chosen to test the method of measurement proposed.

Huntington and Desch have very recently (April 28, 1908) read a paper before the Faraday Society on the "Planimetric Analysis of Alloys," and their work has come to the author's notice since his own results were obtained. They consider the planimetric measurement of the areas to be more accurate and preferable to weighing. The present author considers the weighing method to be preferable for many kinds of structure, and to be susceptible of considerable accuracy. The author is using it for the measurement of rate of change in copper-zinc alloys.

131. "*Viscosity Determinations at High Temperatures.*" By CHARLES EDWARD FAWSITT.

The viscosity of some fused salts and metals has been measured by the method recently described by the author (*Proc. Roy. Soc.*, 1908), lxxx., A, 290). The absolute viscosities of sodium nitrate, potassium nitrate, sodium chloride, potassium chloride, sodium bromide, potassium bromide, and lithium chloride have been determined over a considerable range of temperature. The best comparison of the viscosities of salts is obtained by choosing in all cases the values at the melting-points, or at temperatures easily equally distant from the melting-points. The viscosity of a sodium salt at its melting-point is very nearly the same as the viscosity of the corresponding potassium salt. The viscosity of the salts examined was in no case greater than 0·03 (C.G.S. units); as the viscosity of water at 20° is 0·01, the viscosity of these salts is really not so much greater, as might have been expected. The viscosity of a mixture of sodium and potassium nitrates shows a maximum value at the composition corresponding with the eutectic mixture, provided the comparison is made at temperatures equally distant from the melting-points. The viscosity of a salt decreases with rise of temperature. The temperature coefficients of these salts are proportional to their viscosities. Metals have also a small viscosity. Lead and tin at their melting-points are only about three times as viscous as water. Bismuth and mercury have only about twice the viscosity of water. When a molten metal is cooled to its solidfying-point, there is no abrupt or large increase in the viscosity to indicate the approach of the solid state. The change from the liquid to the solid state corresponds with a sudden and violent change in viscosity.

132. "*Dinitrodiphenylamine-o-sulphonic Acids.*" (Preliminary Note). By SAMUEL SMILES.

By heating 2-chloro-5-nitrobenzenesulphonic acid with the nitroanilines, the corresponding diphenylamine-*o*-sulphonic *acids* are formed. The acids may be isolated as the sparingly soluble, yellow *sodium* salts in a yield equal to about 20 to 25 per cent of the theoretical. These substances have been prepared with a view to effecting the synthesis of the diphenylamine sulphoxides.

133. "*The Study of the Absorption Spectra of the Hydrocarbons Isolated from the Products of the Action of Aluminium Chloride on Naphthalene.*" By ANNIE HOMER and JOHN EDWARD PURVIS.

In an investigation of the action of aluminium chloride on naphthalene, one of the authors isolated, besides Friedel and Crafts' $\beta\beta$-dinaphthyl, three new hydrocarbons, $C_{14}H_{16}$, $H_{26}H_{22}$, and $C_{40}H_{26}$ (*Trans.*, 1907, xci., 1103). In the hope of obtaining additional evidence as to the constitution of these substances, a comparative study of their absorption spectra with that of naphthalene has been made. The absorption spectrum of the hydrocarbon $C_{26}H_{22}$, which was supposed to be an alkyl derivative of dinaphthanthracene, $C_{22}H_{14}$, has also been compared with those of dinaphthanthracene and picene.

The absorption curves for these hydrocarbons show that:—

1. The hydrocarbon $C_{14}H_{16}$ is a naphthalene derivative.
2. The hydrocarbon $C_{40}H_{26}$ has a constitution similar to that of $\beta\beta$-dinaphthyl.
3. The isomeric hydrocarbons, picene and dinaphthanthracene, have markedly different absorption curves.
4. The hydrocarbon $C_{26}H_{22}$ is an alkyl derivative of picene and not of dinaphthanthracene, as had been previously suggested.

134. "*The Synthesis and Constitution of certain Pyranol Salts related to Brazilein and Hæmatein.*" By WILLIAM HENRY PERKIN, jun., ROBERT ROBINSON, and (in part) MAURICE RUSSELL TURNER.

The authors have continued the work of which a preliminary account has already appeared (*Proc.*, 1907, xxiii., 149).

135. "*Brazilin, Hæmatoxylin, and their Derivatives.* Part IX. *On Brazilein, Hæmatein, and their Derivatives.*" By PAUL ENGELS, WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

The authors have continued the investigation of which a preliminary account has already appeared (*Proc.*, 1907, xxiii., 166, 291).

136. "*The Effect of Constitution on the Optical Activity of Nitrogen Compounds.*" By REGINALD W. EVERATT.

Three substituted ammonium iodides containing the *n*-butyl group, namely, phenylmethyl-*n*-butylallyl, *p*-bromophenylbenzylmethyl-*n*-butyl, and *p*-bromophenylmethyl-*n*-butylallylammonium iodides, and also *p*-bromophenylbenzylmethylallylammonium iodide, have been resolved. The first three were required to fill up gaps in the series already examined (Thomas and Jones, *Trans.*, 1906, lxxxix., 280; Jones and Hill, *Trans.*, 1908, xciii., 295), whilst the fourth was needed for purposes of comparison with the phenylbenzylmethylallylammonium iodide of Pope and Peachey (*Trans.*, 1899, lxxv., 1127). The camphorsulphonic acids failed to effect resolution in the case of the third compound mentioned, which was successfully accomplished by means of both camphoric and tartaric acids.

The values obtained for the ammonium salts containing the radicles named are as follows:—

	$[M]_D$ for basic ion.	$[M]_D$ for iodide in alcohol.	$[M]_D$ for iodide in chloroform.
Phenylmethyl-*n*-butylallyl	85·6°	105·1°	123·0°
p-Bromophenylmethyl-*n*-butylallyl	98·0°	114·3°	187·9°
p-Bromophenylbenzylmethyl-*n*-butyl ..	−308·7°	−354·2°	−481·5°
p-Bromophenylbenzylmethylallyl	−191·1°	−242·1°	−346·0°

In all the cases previously examined, the value of $[M]_D$ for the iodide in chloroform is greater than in alcohol; $[M]_D$ for the iodide in alcohol is greater than $[M]_D$ for the ion in water, and the chloroform solution becomes inactive, owing to racemisation.

These relations hold in the above cases, which were, however, peculiar in that the rapidity of racemisation in chloroform was much greater than usual, none of the above compounds requiring more than twenty-four hours, and some considerably less, for complete racemisation.

137. "*The Electrolytic Oxidation of some Hydroxybenzoic Acids.*" By ARTHUR GEORGE PERKIN and FREDERICK MOLLWO PERKIN.

Sodium purpurogallincarboxylate, $C_{11}H_7O_5{\cdot}CO_2Na,4H_2O$, obtained by the electrolytic oxidation of gallic acid, forms orange-brown leaflets, and this with potassium acetate gives the *potassium* salt, $C_{11}H_7O_5{\cdot}CO_2K,3H_2O$, crystallising in prismatic needles. The *barium* salt, $(C_{12}H_7O_7)_2Ba$, crystallises similarly.

Methyl tetramethylpurpurogallincarboxylate,—

$$C_{12}H_3O_7(CH_3)_5,$$

forms pale yellow needles, m. p. 120—121°, and on hydrolysis furnishes the *acid*, $C_{12}H_4O_7(CH_3)_4$, yellow needles, m. p. 182—183°. Purpurogallincarboxylic acid by boiling with concentrated potassium hydroxide solution is converted into *purpurogallonecarboxylic acid*, $C_{11}H_7O_5{\cdot}CO_2H$, yellow needles melting above 360°, which separate both in the anhydrous form and with two molecules of water. On acetylation, *acetylanhydropurpurogallonecarboxylic acid*, $C_{12}H_4O_6{\cdot}(C_2H_3O)_2$, is produced in colourless needles, m. p. 236—238°, which on hydrolysis is reconverted into purpurogallonecarboxylic acid.

Methyl tetramethylpurpurogallonecarboxylate,—

$$C_{11}H_3O(O{\cdot}CH_3)_4{\cdot}CO_2{\cdot}CH_3,$$

colourless prisms, m. p. 110—111°, and the corresponding *acid*, $C_{12}H_4O_7(CH_3)_4$, prisms, m. p. 166—167°, were described. By the electrolytic oxidation of gallic acid in

60 per cent sulphuric acid (compare D.R.-P. 85390), flavellagic acid, $C_{14}H_6O_9$ (*Trans.*, 1906, lxxxix., 251), is obtained, whereas protocatechuic acid gives catellagic acid, $C_{14}H_6O_6$ (*loc. cit.*), but the yields do not compare favourably with those previously obtained by means of persulphates. The best results with gallic acid were obtained by employing a platinum tube as anode and passing cold water through it, using a divided cell. A current density of 0·22 ampère per square centimetre at 7—8 volts was employed, and the yield of flavellagic acid varied from 35 to 40 per cent.

For the preparation of sodium purpurogallincarboxylate, the electrolyte employed was 15 per cent sodium acetate, and the best results were obtained without the employment of a divided cell. The solution was vigorously agitated during the electrolysis, the current density being 0·75 ampère per square dcm. and the E.M.F. 5 to 6 volts.

138. "*Note on Morindin.*" By Arthur George Perkin.

Morindin (*Morinda citrifolia*) according to Oesterle and Tisza (*Arch. Pharm.*, 1907, ccxlv., 534) possesses the formula $C_{27}H_{30}O_{15}$, not $C_{26}H_{28}O_{14}$ as suggested by Thorpe and Greenall (*Trans.*, 1887, li., 52), and gives an acetate, $C_{27}H_{21}O_{15}(C_2H_3O)_9$, m. p. 236—237°, readily soluble in alcohol. An examination of morindin (*Morinda umbellata*) by the author gave results agreeing with the older formula, $C_{26}H_{28}O_{14}$ (found, C = 55·37; H = 5·14). The acetyl derivative, prepared by adding pyridine to the substance in acetic anhydride and boiling for three hours, forms pale yellow needles, m. p. 246—248°, very sparingly soluble in alcohol, and possessing the formula $C_{26}H_{20}O_{14}(C_2H_3O)_8$ (found, C = 56·01; H = 5·14, and, on hydrolysis, acetic acid = 53·60, morindone = 29·84, 29·99). The morindone thus produced was pure (found, C = 66·64; H = 3·90). Morindin acetate was unaltered by long digestion with acetic anhydride, and was also formed when the method given by Oesterle and Tisza (*loc. cit.*) was employed. The sugar obtained by hydrolysis of the glucoside gave an osazone, m. p. 202—203°, sparingly soluble in alcohol, whereas that described by Oesterle and Tisza is readily soluble, and melts at 197°. Independent analyses of morindin carried out for the author at the University, Manchester, gave C = 55·10, 55·10; H = 5·00, 5·20 per cent, and it thus seems likely that the morindin present in the *Morinda citrifolia* is not identical with that contained in the *Morinda umbellata*.

139. "*Some Esters of Arsenious Acid.*" By William Robert Lang, John Francis Mackey, and Ross Aitken Gortner.

The authors have heated a number of alcohols and phenols in contact with arsenious oxide, using a reflux condenser with a Soxhlet attachment containing anhydrous copper sulphate to remove the water formed in the reaction $6ROH + As_2O_3 = 2R_3AsO_3 + 3H_2O$, otherwise a condition of equilibrium is set up at a point where only a small portion of ester has been formed. Anhydrous copper sulphate has also been employed mixed with the alcohol and arsenious oxide in the cold with good results. The following esters have been prepared in large quantities; they all decompose with water, and are capable of dissolving considerable amounts of the arsenious oxide:—

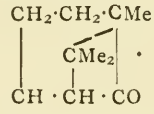
Percentage Yield with Anhydrous Copper Sulphate.

	In Soxhlet.	Mixed together cold.
Propyl arsenite	56·75	14·8
*iso*Butyl arsenite	56·25	15·8
Trimethylcarbinol arsenite	54·27	—
Amyl arsenite	54·00	—
*iso*Amyl arsenite	58·62	17·2
Phenyl arsenite	60·00	—

Yields of 33·8 per cent and 4·5 per cent of methyl and ethyl arsenites respectively were obtained also, and it is found that ethyl alcohol has a much greater attraction for water than methyl or the higher alcohols, which accounts for the smallness of the yield in its case. In addition to those mentioned above, esters with the three cresols, naphthol, benzyl alcohol, the dihydric and trihydric phenols, and with methyl salicylate have all been prepared, but not quantitatively; the reaction takes place very readily. A method of analysis for the phenyl ester by titration with iodine and with dichromate was worked out and gives accurate results.

140. "*α-Methylcamphor and Fenchone.*" By Walter Hamis Glover.

The general chemical behaviour of α-methylcamphor has been contrasted with that of fenchone, and it is shown that the two substances are essentially different; thus, α-methylcamphor, unlike fenchone, is readily brominated, yielding α′-bromo-α-methylcamphor (Minguin, *Comptes Rendus*, 1903, cxxxvi., 751), and is also easily converted into a β-sulphonic acid. Fenchone, therefore, cannot possess the constitution assigned to it by Wallach (*Annalen*, 1898, ccc., 319); objections may also be raised to Semmler's formula (*Chem. Zeit.*, 1905, xxix., 1313). It is suggested that the following formula better represents the behaviour of fenchone:—



The following new derivatives of α-methylcamphor have been prepared; they are very similar to the corresponding derivatives of *d*-camphor.

α′-Bromomethyl-α-methylcamphor, $C_{10}H_{14}Br(CH_2Br)O$, crystallises in colourless, silky needles, m. p. 108—109°, $[\alpha]_D$ 20 +117·5° in benzene. *α-Methylcamphor-β-sulphonic acid*, $C_{10}H_{14}MeO{\cdot}SO_3H$, forms large, deliquescent, colourless prisms, m. p. 114—116° (decomp.), $[\alpha]_D$ 20 +18·7° in water; the *barium* salt, $(C_{11}H_{17}O_4S)_2Ba,6H_2O$, forms large, thick, transparent, hexagonal plates, m. p. 66°; the *sulphonyl chloride*, $C_{11}H_{17}O{\cdot}SO_2Cl$, crystallises in transparent, prismatic needles, m. p. 33°, $[\alpha]_D$ 20 +29·5° in benzene; the *sulphonamide*, $C_{11}H_{17}O{\cdot}SO_2{\cdot}NH_2$, crystallises in long, silky needles, m. p. 150°, $[\alpha]_D$ 20 −6·3° in chloroform; the *sulphonanhydramide*, $C_{11}H_{15}ONS$, is a fine, crystalline powder, m. p. 167·5°. *β-Bromo-α-methylcamphor*, $C_{11}H_{17}OBr$, crystallises in white, silky needles, m. p. 55°, $[\alpha]_D$ 25 +18·8° in ethyl alcohol. *α-Methylcamphoroxime*, $C_{11}H_{18}{:}NOH$, crystallises in long, slender needles, m. p. 55°, $[\alpha]_D$ 20 +30·3°; the *hydrochloride*, $C_{11}H_{19}ON,HCl$, forms silky needles, m. p. 138° (decomp.). *Methylcampholenonitrile* is an oil with a peppermint-like odour, b. p. 226—228°.

141. "*Ester Hydrolysis and Theories of Esterification.*" By Arthur Lapworth.

The author has recently pointed out (*Proc.*, 1908, xxiv., 101) that, whilst the initial velocity of hydrolysis of ethyl formate in acetone with hydrogen chloride as catalyst is roughly proportional to the respective concentrations of mineral acid and ester, it is hardly dependent on the amount of water present within a range of 4—20 per cent, and concluded that this afforded definite proof of the incorrectness of the theory advanced by Stieglitz, which demands a proportionality between the velocity and the concentration of the water. This conclusion was erroneous, because the possibility remains that the water so affects the medium (compare following Note) that the effects due to its possible depressing effect on the reaction velocity, to the altered ionisation of the mineral acid, and to its own increased concentration exactly neutralises one another. It must be noted that the striking coincidence must be assumed to apply in alcoholic solution within similar

limits as the results of Kistiatowski show (*Zeit. Phys. Chem.*, 1898, xxvii., 253 *et seq.*).

Reference must here be made to the experiments of Ostwald (*Journ. Prakt. Chem.*, 1883, [ii.], xxviii., 463), in which the effect of replacing some of the water by acetone during ester catalysis was found to be very small.

The observed increase on the velocity of catalysed esterification with increase of alcohol concentration in acetone and water (see following Note), as well as in water (van 't Hoff; Kistiatowski), makes it appear very probable that the suggestion of Acree and Johnson (*Am. Chem. Journ.*, 1907, xxxviii., 344), namely, that the alcohol and water enter into these reactions as neutral components in a complex ion formation, is correct; as an alternative it is possible (Stieglitz, *Ibid.*, 1908, xxxix., 60; Acree and Johnson, *loc. cit.*) that both ions of these compounds act simultaneously, but this seems less acceptable. It is not necessary, however, *a priori*, either for chemical or mathematical reasons, to suppose that during reactions in which carbonyl compounds take part under the influence of mineral acids it is the instantaneously formed oxonium ions which are directly concerned, and the fallacy in this assumption is obvious when it is remembered that the measured velocity of bromination of acetone (*Trans.*, 1904, lxxxv., 31 *et seq.*) is that of a change induced in the carbonyl compound itself by the mineral acid before the bromine enters into the reaction at all; something similar is not excluded in esterification.

142. "*Experiments on the Formation and Hydrolysis of Esters, Acetals, and Allied Compounds.*" (Preliminary Note). By Edward Fitzgerald and Arthur Lapworth.

At 18·2°, the initial velocity of hydrolysis of methyl acetate is nearly independent of the concentration of the water within the limits 4—30 per cent in acetone.

During esterification by ethyl alcohol in acetone or ether, the velocity for a short time is roughly proportional to the concentration of the alcohol. In acetone, which appears to take no part in the reaction, alcohol depresses the initial velocity of hydrolysis of methyl acetate, but the effect of water on the reverse reaction is much greater, and the speed of esterification of acetic acid is, very roughly, inversely proportional to the concentration of water within the limits 4—20 per cent. This appears to lend considerable support to the supposition that the velocity of hydrolysis of an ester is intrinsically proportional to the concentration of the water, but is proportionately depressed by its action on the medium and the ionisation of the hydrogen chloride, but this leaves no room for the depression which water might produce on the velocity of esterification by sharing the intermediate products with the alcohol. (Depression of the velocity of esterification by water was noticed by Goldschmidt, Kistiatowski, and others).

Methods of estimating the speed of hydrolysis of acetals and of ethyl orthoformate have been devised. The latter is hydrolysed by N/1000 hydrochloric acid at a speed which is too great to be followed, but in N/5000 hydrochloric acid (or in N/10 acetic acid to which an equivalent of sodium acetate has been added) the change into alcohol and ethyl formate can be traced; the velocity is more than 10,000 times as great as that of the hydrolysis of ethyl formate.

In all the above experiments, hydrogen chloride was used as catalyst, and the temperature was constant within 0·05°.

The equilibrium "constant" for esterification in acetone shows irregularities similar to those seen when acetone is absent, the proportion of ester being altered to an unexpectedly small extent by addition of excess of alcohol.

It is hoped that the ionisation factor of hydrogen chloride in the media employed having been ascertained, a further study of the reactions will throw some light on these questions.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvi., No. 22, June 1, 1908.

Hydrates of Fatty Acids.—D. E. Tsakalotos.—The study of the coefficients of viscosity of binary systems provides a simple and very sensitive method of detecting the existence of molecular compounds in the liquid state, even when these compounds undergo partial dissociation. From experiments with formic acid it is found that, although pure formic acid has a higher coefficient of viscosity than its homologues, aqueous solutions of the acid have much lower coefficients than corresponding solutions of other acids of the fatty series. The coefficients of viscosity of the system HCOOH and H_2O are rather lower than those calculated by the law of mixtures, while other systems have much higher coefficients than the calculated values. The study of the coefficients shows that no compound of formic acid and water exists, while acetic, propionic, and butyric acids form molecular compounds: $CH_3COOH + H_2O$, $CH_3CH_2COOH + H_2O$, $CH_3CH_2CH_2COOH + H_2O$.

Action of Ammonia on Chlorphosphamide.—MM. Besson and Rosset.—Stokes has shown that a solution of ammonia acts on an ethereal solution of chlorphosphamide giving an amide derivative, $P_3N_3Cl_4(NH_2)_2$. When liquefied ammonia is used in absence of water the product has the formula PN_3H_4, and apparently the equation is $PNCl_2 + 4NH_3 = 2NH_4Cl + PN(NH_2)_2$. When $PN(NH_2)_2$ is heated to 220° for several days it loses NH_3, and its composition approaches that of Gerhardt's phosphamide, $PN(NH_2)_2 = NH_3 + PN_2H$. With gaseous ammonia in absence of water the substance obtained has the formula $P_2N_3Cl_5(NH_2)2PNCl_2 + 2NH_3 = NH_4Cl + P_2N_2Cl_3(NH_2)$. When the raw product is extracted with carbon tetrachloride a white insoluble residue remains, which does not appear to be a definite compound but a mixture of NH_4Cl and $PN(NH_2)_2$. The reaction of gaseous ammonia upon phosphamide can be represented by the equation $(PNCl_2)_3 + 6NH_3 = P_2N_2Cl_3NH_2 + 3NH_4Cl + PN(NH_2)_2$. Soluble in CCl_4. Both insoluble in CCl_4. The first substance is obtained at a low temperature in presence of a limited amount of NH_3 and the second with excess of the gas.

Phosphoric Acid Ethers of Guaiacol.—V. Auger and P. Dupuis.—The authors have obtained acid phosphates containing one or two molecules of guaiacol to one molecule of H_3PO_4 by three methods:—1. By boiling phosphorus oxychloride with guaiacol; according to the conditions of the reaction the product obtained is the dichloride of guaiacol phosphoryl, the chloride of diguaiacol phosphoryl, or the neutral phosphate of guaiacol. The hydrolysis of the chlorides gives the corresponding acids. 2. By allowing phosphorus oxychloride to react on a mixture of guaiacol and pyridine in the cold. The salt of pyridine obtained when decomposed by an alkali gives salts of the ether acids formed. 3. By saponifying with alcoholic soda the neutral phosphate of guaiacol.

Mechanism of Formation of Cyclic Compounds in Geranic Series. Synthesis and Structure of Dihydromyrcene.—M. Tiffeneau.—The condensation of methylheptanone in presence of zinc or magnesium, either with ethyl-α-bromopropionate or ethyl α-chloropropionate, gives the ethyl ether of oxydihydro-α-methyl geranic acid, which yields α-methyl geranic acid on saponification, $(CH_3)_2{:}C{:}CH.(CH_2)_2.CCH_3{:}C(CH_3).CO_2H$. When distilled slowly at the ordinary pressure the acid loses CO_2, and gives dihydromyrcene, $(CH_3)_2{:}C{:}CH(CH_2)_2.C(CH_3){:}CH.CH_3$. This hydrocarbon is identical with Enklaar's dihydroocimene. This synthesis

confirms Enklaar's conclusions on the nature of the terminal chain, $(CH_3)_2C=$, and shows that the dehydration of oxydihydromethyl geranic acid is effected at the expense of the neighbouring carbon atom.

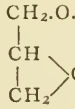
Berichte der Deutschen Chemischen Gesellschaft.
Vol. xli., No. 7, 1908.

Action of Dimethylsulphate on Alkaline Polysulphides.—W. Strecker.—Dimethylsulphate reacts very energetically with alkaline polysulphides, and when sodium pentasulphide is used an oil is obtained which contains approximately the amount of sulphur shown by the formula $(CH_3)_2S_5$. If the raw product is distilled under diminished pressure both from preparations derived from sodium penta- and tetrasulphides, methyltrisulphide is obtained.

Glycerin Nitrates.—W. Will.—When dinitroglycerin is prepared by Mikolajczak's method the resulting oil is a mixture of the two stereo-isomers :—

$$\begin{matrix}CH_2.O.NO_2\\ CH.OH\\ CH_2.O.NO_2\end{matrix} \quad \text{and} \quad \begin{matrix}CH_2.O.NO_2\\ CH.O.NO_2\\ CH_2.OH\end{matrix} .$$

They may be separated as follows:—The oil is allowed to absorb water from the air, and is then mixed with kieselguhr, and cooled. After some time crystallisation ensues. If traces of this solidified mixture are introduced into dinitroglycerin which has been exposed to the air, large clear prismatic crystals are at once formed. Small quantities of an oil remain, and the author has shown that the crystallising portion consists of one of the isomers and the oil of the other; he calls the former "Dinitroglycerin K" and the latter "Dinitroglycerin F." Both forms yield trinitroglycerin when nitrated, and from both of them the same mononitroglycide,—



can be obtained. Similarly, mononitroglycerin exists in two stereoisomeric forms, of which β-form yields only dinitroglycerin F when cautiously nitrated. The α-form fuses at 58° and the β-form at 54°. From the results of the author's experiments it is evident that the mononitrate fusing at 58° has the formula—

$$\begin{matrix}CH_2.O.NO_2\\ CH\cdot OH\\ CH_2.OH\end{matrix} ,$$

while the β-form (melting-point, 54°) is—

$$\begin{matrix}CH_2.OH\\ CH.O.NO_2,\\ CH_2.OH\end{matrix}$$

The dinitrate, which does not crystallise, is—

$$\begin{matrix}CH_2.O.NO_2\\ CH.O.NO_2\\ CH_2.OH\end{matrix} ,$$

and the crystallising dinitrate is—

$$\begin{matrix}CH_2.O.NO_2\\ CH.OH\\ CH_2.O.NO_2\end{matrix} .$$

The following table shows the chief properties of glycerin and its nitrates :—

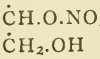
Glycerin—	
Specific gravity (15°)	1·27
Melting-point	17°
Boiling-point (15 mm.)	150—160°
Solubility in water at 15°	Unlimited.
Heat of combustion (H_2O liquid)	4317 cals.
Mononitrate—	
Specific gravity (15°)	1·40
Melting-point: α-Nitrate	58°
Melting-point: β-Nitrate	54°
Boiling-point (15 mm.), both isomers	155—160°
Solubility in water at 15°	70 per cent
Heat of combustion (H_2O liquid), α-nitrate	2812 cals.
Dinitrate—	
Specific gravity (15°)	1·47
Melting-point: α-Hydrate	26°
Melting-point: β-Hydrate	Liquid.
Boiling-point (15 mm.), both isomers	About 145°
Solubility in water at 15°	7·7 per cent
Heat of combustion (H_2O liquid): K, dried	2088 cals.
Heat of combustion (H_2O liquid): K, cryst.	1986 „
Heat of combustion (H_2O liquid): F	2055 „
Trinitrate—	
Specific gravity (15°)	1·60
Melting-point: Labile modification	2·2°
Melting-point: Stable modification	12·2°
Boiling-point (15 mm.)	Evaporates rapidly at 160° without boiling.
Solubility in water at 15°	0·16 per cent.
Heat of combustion (H_2O liquid)	1570 cals.

Constitution of Carbon Suboxide.—Otto Diels and Paul Blumberg.—The authors believe that the constitutional formula of carbon suboxide is not that ascribed to it by Michael,—

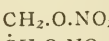
$$C\equiv C-\!>O,$$
$$\quad\quad CO$$

but the symmetrical formula $C\begin{matrix}\equiv CO\\ \equiv CO\end{matrix}$. The reasons they give for their opinion are as follows:—1. The boiling-point of the compound is 7°. 2. The compound resembles the metallic carbonyls. 3. The values of the molecular refraction and dispersion are high. 4. The compound shows great resemblances to ketenes. 5. Four atoms of bromine readily add themselves on, and the compound can be prepared from dibrommalonylbromide. 6. It is very improbable that a β-lactone with a triple bond exists. 7. The addition of water gives only malonic acid.

New Synthesis of Isoxazoles.—Julius Schmidt and Karl Th. Widmann.—By the action of red fuming nitric acid on β-diacetosuccinic acid ethyl ester at a temperature of from 0° to 5°, a fairly good yield of a compound with the empirical formula $C_{10}H_{13}NO_5$ is obtained. This is found to be α-methyl β-isoxazole γ-dicarbonic acid ethyl ester, $CH_3.C{:}C.COOC_2H_5$



. The ester can be saponified by shaking with caustic soda solution, yielding α-methyl β-isoxazole γ-dicarbonic acid, from which the α-methyl isoxazole,



, can with difficulty be isolated by distillation.

Decomposition of Antimony Hydride.—Alfred Stock, Eusebio Echeandia, and Paul R. Voigt.—The investigation of the decomposition of antimony hydride at 0°, 25°, 50°, and 75° shows that at all four temperatures the variation in the velocity of the reaction is given by the equation $\Lambda = \frac{1}{C^{1-p}}$, where C is the concentration of the hydride in the space containing the gas and p is a constant.

The coefficient β increases as the temperature rises. All the phenomena observed agree with the assumption that the decomposition of the hydride occurs only in the layer adsorbed on the surface of the antimony.

Decomposition of Arsenic Hydride.—Alfred Stock, Eusebio Echeandia, and Paul R. Voigt.—The investigation of the decomposition of arsenic hydride is difficult, because the compound is split up only at comparatively high temperatures. Nevertheless, the authors have succeeded in showing that as the concentration of arsenic hydride falls the velocity of decomposition increases. This result agrees with the assumption that the reaction occurs only in the adsorbed layer.

Reactions of Pyridine.—Hans Th. Bucherer and Julius Schenkel.—When pyridine is subjected to the action of sodium bisulphite very labile derivatives are formed, which appear to be sulphurous acid esters. These are soluble in water and are not volatile in steam. They are characterised by the ease with which they are attacked by alkalis, which split off all the nitrogen in the form of ammonia in the cold. The authors have not yet completed the investigation of the action of bisulphite solutions on the homologues and isomers of the pyridine series. If a mixture of different homologues and isomers of pyridine bases is treated with excess of bisulphite solution, the product consists of soluble addition products and of insoluble or difficultly soluble pyridine bases; it may then be treated with water vapour, ether, or benzene to separate the original mixture into two different parts.

Reaction between Indigotin and Potassium Permanganate.—O. Miller and J. Smirnoff.—Mohr found that when indigotin is oxidised with potassium permanganate, 316·2 parts of permanganate oxidise 750 parts of indigotin, whereas the amount of the latter theoretically oxidised is 655 parts. The authors have repeated the titrations, using specially purified natural and synthetic indigo from which to obtain the indigotin, and they have arrived at a result which agrees with Mohr's, viz., that the oxygen used up is a constant amount (12·6 per cent) too small. The cause of this phenomenon does not lie in the composition of the indigotin. The authors have observed that when indigotin is sulphated no sulphurous acid is evolved, nor is the oxygen of the air taken up by the product of the reaction.

Red Phosphorus.—G. Linck and P. Möller.—When purified dried red phosphorus is sublimed at the melting-point of lead in an exhausted glass tube a black brittle mass, which shows no trace of crystallisation, is obtained. In thin fragments it appears red, and it contains 99·4 per cent of phosphorus. The specific gravity determinations gave results which varied from 2·145 to 2·192 at 18—20°, and this agrees almost exactly with that of commercial red phosphorus. By prolonged heating in a closed tube both forms can be converted into the crystalline form, the powder becoming a light red. From this it appears that a modification of phosphorus exists which is labile as regards the densest known form, and which possibly forms the isotropic amorphous phase, corresponding to red crystalline phosphorus. Mixtures of arsenic and phosphorus can readily be obtained if red phosphorus and metallic arsenic are sublimed together; the product of the sublimation exhibits a conchoidal fracture and a black metallic lustre, and in very thin splinters appears brown in transmitted light. The specific gravity varies between fairly wide limits according to the percentage composition.

Reduction with Platinum and Hydrogen at the Ordinary Temperature.—Richard Willstätter and Erwin W. Mayer.—Substances which are not volatile enough, or are too easily decomposed to be led over nickel, can readily be reduced by hydrogen in presence of platinum. This method can be applied to compounds containing the difficultly reducible ethylene bond. From phytene the saturated hydrocarbon phytane, $C_{20}H_{42}$, is obtained Benzoic acid slowly takes up hydrogen in ethereal solution, and the hexahydro-compound is formed. Unsaturated alcohols, *e.g.*, erucyl alcohol, give saturated alcohols, or, as in the case of genaniol, a mixture of saturated alcohol and saturated hydrocarbon.

Hexathiocyanate Salts of Molybdenum.—Johanna Maas and J. Sand.—When a solution of ammonium molybdate and ammonium thiocyanate in hydrochloric acid is reduced electrolytically with platinum cathodes, from the reduced solution after a time yellow crystals separate out in the cold. These have the formula—

$$\overset{IV}{Mo}(SCN)_6\begin{matrix}NH_3H\\NH_3H\\NH_3\\OHH\end{matrix}+3H_2O.$$

The ammonium salt forms a very characteristic acetate, $[\overset{IV}{Mo}(SCN)_6(NH_3)_3HOH\,\underset{CH_3.COOH}{H_2}$. By the electrolytic reduction of hydrochloric acid solutions of potassium molybdate-potassium thiocyanate a very pure potassium salt can be isolated, containing the group $Mo(SCN)_6R_3$. Besides loosely bound water of crystallisation the salt contains a firmly bound oxygen atom for each molybdenum atom. Hence it might be supposed that trivalent molybdenum is present and one aquo molecule is contained in the complex, *i.e.*, the formula is $[\overset{III}{Mo}(SCN)_6H_2O\,K_3+4H_2O$. If a hydrochloric acid green solution of pure molybdenum trichloride is used as the starting-point, only traces of the salts of the yellow series are formed. Hence tetravalent molybdenum is undoubtedly present, and the structural formula is—

$$\begin{matrix}R—SCN\,----\,IV.\,\overset{'\,'\,'\,'}{}\,SCN\\R—SCN\,----\,Mo\,\overset{'\,'\,'\,'}{}\,SCN\\R—SCN\,----\,\underset{OH}{|}\,\overset{'\,'\,'\,'}{}\,SCN\end{matrix}+4H_2O.$$

In all the derivatives of the yellow series the hydroxyl group can be detected, and thus apparently the hexathiocyanate compounds belong to the class of hydroxo-salts; possibly they are allied to Werner's "*ol*" salts. This hydroxyl, however, does not possess the well marked basic properties of the hydroxyl in the typical hydroxo-salts of cobalt. The hydrohexathiocyanate salts, especially the ammonium and potassium salts, give with acids addition products, which are split up into their components in aqueous solution. The co-ordination number of tetravalent molybdenum appears to be 8. The formula of the potassium salt-acetate is given in the original paper.

MISCELLANEOUS.

Albert Medal of the Royal Society of Arts.—The Albert Medal of the Royal Society of Arts for the present year has been awarded, with the approval of His Royal Highness the President, to Sir James Dewar, M.A., D.Sc., LL.D., F.R.S., "For his investigations into the liquefaction of gases and the properties of matter at low temperatures, investigations which have resulted in the production of the lowest temperatures yet reached, the use of vacuum vessels for thermal isolation, and the application of cooled charcoal to the separation of gaseous mixtures and to the production of high vacua."

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Carbon Tetrachloride.—A correspondent would be glad to know who are the makers of carbon tetrachloride.

INDEX.

"ACCOUNTS, Process Cost" (review), 287
Acetals, formation and hydrolysis of, 310
Acetamide preparation, 104
Acetate, mercuric, and diazomethane, action of, 166
Acetone and malonic acid, $\alpha\beta$-lactonic acid from, 94
Acetoxime, influence of acids and alkalis on velocity of formation of, 11
Acetoxy-ketones, β-, constitution, 46
Acetylation of amino-groups, 273
Acetylene and calcium carbide, synthesis, 167
Acetylketen, 247
Acid, aminopinenedicarboxylic, condensation products from, 307
anhydrobrazilic, synthesis of, 129
arsenic, hydrates of, 239
arsenious, esters of, 309
benzoyl acrylic, fixation of hydrocyanic acid by, 276
brazilinic, synthesis, 129
bromic, oxidation phenomena produced by, 299
carbonic, and other acids, determining simultaneously in atmospheric air, 299
cyanoacetic, action of mustard oils on ethyl esters of, 129
diglycollic, homologues of, 72
dihydrobrazilinic, synthesis of lactones of, 129
dihydrocamphoric, synthesis of racemic, 117
dihydrohæmatoxylinic, synthesis of lactones of, 129
gallotannic, constitution, 133
hydrochloric, and aluminium chloride, products of action of on benzene, 239
hydrocyanic, fixation by benzoyl acrylic acid, 276
hypoiodous, action of nascent upon acids of formula $R-CH=CH-CH_2-CO_2H$, 119, 179
hyponitrous, decomposition, 82
hypovanadic, isomeric modification of hydrated, 179
iodic, oxidation phenomena produced by, 299
$\alpha\beta$-lactonic from acetone and malonic acid, 94
malonic, action of mustard oils on ethyl esters of, 129
and acetone, $\alpha\beta$-lactonic acid from, 94
1-methylcyclohexylidene-4-acetic, synthesis of, 307
molybdic and vanadic acid, determination in presence of one another, 245
behaviour in the zinc reductor, 113
nitric, and copper, interaction in presence of metallic nitrates, 306
nitrous, action on allylamine, 46
oleic, conversion into candle material, 238
γ-oxytetrolic, 143
para-dimethylamido-ortho-benzoyl benzoic, action of phenyl magnesium bromide on the second methyl ether of, 276
1-phenylchloroacetic, displacement of halogen in by hydroxy- and methoxy-groups, 235
Acid, succinic, esterification, use of zinc chloride in, 112
sulphosalicylic, action on borax, 179
tartaric, detection in cider, 47
determining, volumetric method, 299
titani-dihydroxymaleic, and detection of titanium, 273
tungstic, determination and separation from other substances, 299
vanadic, and molybdic acid, determination in presence of one another, 245
Acids as accelerators in acetylation of amino-groups, 273
influence on velocity of formation of acetoxime, 11
of formula—
$R-CH=CH-CH_2-CO_2H$,
action of nascent hypoiodous acid upon, 119, 179
acetylenic, formation of 4-pyrone compounds from, 128
arsonic and arsinic, aromatic, 307
atrolactic and p-methoxyatrolactic, comparative study of, 263
dinitrodiphenylamine-o-sulphonic, 308
ethyl barbituric, electrolytic reduction, 23
fatty, esterification constants of normal, 81
hydrates of, 310
melting-points of the anilides, p-toluidides, and α-naphthalides of normal, 261
hydroxybenzoic, electrolytic oxidation, 308
α-hydroxycarboxylic, action of heat on, 165
mineral, salts of p-hydroxyazo-compounds with, 67
triazoacetic, and α-triazopropionic, dissociation constants of, 259
Actinium, distribution in electric fields of active deposits of, 156
Acyl-salicylamides and acylhydroxylamines, labile isomerism among, 177
"Adulterants, Food, Detection of the Common" (review), 191
Air, causes of variations of carbon dioxide in, 288
charcoal and liquid, 4, 16
determining mercury vapour in, 263
simultaneously carbonic and other acids in atmospheric, 299
ionisation by ultra-violet light, 275
Albahary, J. M., complete analysis of vegetable matter, 152
Albert Medal of the Royal Society of Arts, 312
Alcohols, action of metallic calcium on, 10
on sodium benzylate, 143
aromatic, reactions of, 47
$\beta\alpha\alpha$-dialcoholated ketone, 250
Aldehydes, transformation of α-oxyacids into, 119
cyclic, preparing, 143
Alkali metals, discovery by Davy, 11, 193, 210
heat of solution of, 119
molecular volumes of, 176
Alkalis and alkaline earths, neutral carbonates of, 228
Alkalis and magnesium, separation by alcoholic ammonium carbonate, 280
influence on velocity of formation of acetoxime, 11
Alkaline polysulphides, action of dimethylsulphate on, 311
Alkyl iodides, effects of heat on, 10
Alleman, G., and L. T. Sherwood. (*See* Sherwood, L. T.)
Allmand, A. J., and H. G. Denham. (*See* Denham, H. G.)
Alloys, copper, determination of small percentages of iron in, 10
lead-antimony, determination of antimony and arsenic in, 271
measurement of rate of change in solid, 307
of platinum and thallium, 264
planimetric analysis of, 238
Allylamine, action of nitrous acid on, 46
Allylazoimide, 306
Alternating currents, production of small variable frequency suitable for telephonic and other measurements, 285
Alumina and silica, catalytic power of, 119
in iron ores, determination, 31
Aluminium chloride, action on naphthalene, absorption spectra of hydrocarbons isolated from products of, 308
and hydrochloric acid, products of action of on benzene, 239
iodomercurate, 298
powder and carbon, interaction, 219, 233, 238
Amides, molecular complexity of in various solvents, 247
Amidines, chemistry of, 274
Amido-group attached to the nitrogen atom of heterocyclic compounds, 48
Amino-groups, acids as accelerators in, 273
Ammonia, action on chlorophosphamide 310
order of addition of to organic α-oxides of asymmetric structure, 142
synthesis of, 119
Ammonium and dimercuric ammonium, dissociation of double chlorides of by water, 132
chromate, slow decomposition by heat, 274
dichromate, decomposition by heat, 92, 274
phosphomolybdate, variations in composition of, 263
syngenite, 143
trichromate, slow decomposition by heat, 274
Amygdalin, hydrolysis by emulsin, 246
Analysis, official methods of, 298
"Analysis, Chemical, Complete Treatise of Technical" (review), 71
"Analysis, Chemical, Laboratory Outline for Determinations in Quantitative" (review), 297
"Analysis, Quantitative, Exercises in Elementary" (review), 296
"Analytical Notes" (review), 203
Andersen, N., and L. Pelet-Jolivet. (*See* Pelet-Jolivet, L.)
Anilides of normal fatty acids, melting-points of, 261
Anilidophenosafranine, phenylated, synthesis of symmetrical, 35
2-Anilinobenzoxazole, 274
Anilodihydrobenzoxazole, 274
"Annual for the Year 1903" (review), 84
Anthraquinones, 128
Antimony, determination in lead-antimony alloys, 271
hydride, decomposition, 311
heat of formation, 168
selenide, compounds of silver selenide with, 288
Apparatus for automatic examination of carbon dioxoxide, 286
for demonstrating propagation of alternate current waves in cables, 189
for determining specific inductive capacity of organic liquids, 262
for experiments at high temperatures and pressures, and application to study of carbon, 273
for producing spark spectra of solutions, 35
for simultaneously extracting a solid and filtering the solution so obtained, 280
for sublimation, 198
vapour-density, form of release for Victor Meyer's, 73
Applebey, M. P., H. Hartley, and N. G. Thomas. (*See* Hartley, H.)
Arabinose, l-, preparation, 119
Arbutine and derivatives, 263
Archer, R. M., illustrations of geometrical optics, 249
Arrhenius, S., "Immunochemistry" (review), 83
Arsenic in lead-antimony alloys, determination, 271
hydride, decomposition, 312
selenide, compounds of silver selenide with, 288
Aryl halides and magnesium, interaction, 8
Aschan, O., new borneol, 251
Atkins, W. R. G., freezing-point of milk, 241
Atmosphere, origin of ozone in, 288
Atomic theory, physical aspect of, 109
weight, choice of most probable value for an, 58
of chlorine, 135, 146, 159
europium, 173
hydrogen, 56, 58, 64, 76
radium, 229
tellurium, 25, 209
weights of elements, relations between, 46
report of committee on, 43
symmetry in law of, 99
Auger, V., hydrates of arsenic acid, 239
mixed trihaloid derivatives of methane, 299
new type of compounds of sulphur with certain iodides, 218
preparation of methyl and ethyl cyanides, 47
and P. Dupuis, phosphoric acid ethers of guaiacol, 310
Auld, S. J. M., hydrolysis of amygdalin by emulsin, 246
and T. A. Henry. (*See* Henry, T. A.)
Austenite, 264
Austin, P. C., and A. Senier. (*See* Senier, A.)
Australia, tantalite in, 203

Autenrieth, W., and A. Geyer, reaction between phenols and phosphorus pentachloride, 143
Autolysator, 286
Autoxidation, visible, 167
Azo-compounds, colour and constitution, 67
Azoimides of propionic ester and of methyl ethyl ketone, 129
Azomethine compounds, colour and constitution 91

BAEKELAND, L. H., danger of over specialisation, 106, 114
Baker, H. B., atomic weight of tellurium, 209
J. L., and H. F. E. Hulton, considerations affecting the strength of wheat flours, 190
T. T., "The Spectroscope" (review). 250
Ball, W. C., slow decomposition of ammonium chromate, dichromate, and trichromate by heat, 274
Barbaloin, transformation into β-barbaloin, 35
Barbier, P., and V. Grignard, new method of hydrating pinene, 59
and P. Sisley, synthesis of symmetrical phenylated anilidophenosafranine. 35
Barger, G., action of thionyl chloride and of phosphorus pentachloride on the methylene ethers of catechol derivatives, 128
and A. J. Ewins, action of thionyl chloride on the methylene ethers of catechol derivatives, 153
Barium carbonate, carbon, and nitrogen, influence of addition of chloride to reaction between, 87
oxide, heat of formation of anhydrous, 142
percarbonate, 144
Barker, J. T., physico-chemical study of the complex copper glycocoll sulphates, 11, 37, 51
T. V., note on the iodates and periodates of the alkalis and the ammonium radicle, 10
Barlow-Pope theory of structure, crystal form of halogen derivatives of open-chain hydrocarbons with reference to, 93
Barnett, E. de B., and S. Smiles, note on phenolic thetines and their action with benzoyl chloride, 262
Barrett, E., and A. Lapworth, influence of acids and alkalis on the velocity of formation of acetoxime, 11
Barthe, L., action of sulphosalicylic acid on borax, 179
Baubigny, H., determination of halogens in chloro-brominated organic compounds, 275
oxidation phenomena produced by iodic and bromic acids, 299
separation of silver chloride and iodide, 167
Bauer, E., and A. Haller. (*See* Haller, A.)
Baum, F., preparation of bromine cyanide and cyanamide derivatives, 168
Bay, I., determination of carbon disulphide in benzene, 119
new method of determining phosphorus in organic matter, 258
sulphur in organic matter, 167
Beadle, C., and H. P. Stevens, mode of valuing raw rubber, 73
Becquerel, J., phenomena in the spark spectrum of yttrium attributable to positive electrons, 250
variations of the absorption bands of salts of didymium and erbium in a magnetic field, 49
Becquerel, J., and H. K. Onnes, absorption spectra of crystals of the rare earths salts and their modification in a magnetic field at the melting-point and boiling-point of hydrogen, 239
Beef, New Zealand boned, 50
Belloc, G., gases occluded in steel, 46
Bengough, G. D., method for the measurement of rate of change in solid alloys, 307
Bent, L. N., W. H. Walker, and Anna M. Cederholm. (*See* Walker, W. H.)
Bentley, W. H., and C. Weizmann, researches on the anthraquinones, 128
Benzene, determination of carbon disulphide in, 119
in illuminating gas, determination, 282, 293
products of action of aluminium chloride and hydrochloric acid on, 239
vapours, absorption spectra of, and its homologues, 97
Benzoin, condensation with methyl alcohol, 260
l-, preparation, 92
Benzoyl chloride, action of phenolic thetines with, 262
Benzylethyldipropylsilicane, sulphonation, 69
Benzylethylpropylsilicyl oxide, sulphonation, 69
Benzylethylsilicone, 92
Berger, E., phosphorus oxybromide, 174
Berkhold, O., and O. Kühling. (*See* Kühling, O.)
Bertrand, G., and P. Bruneau, preparation and properties of crystalline *d*-talite, 180
Beryllium. (*See* Glucinum)
Besson and Rosset, MM., action of ammonia on chlorphosphamide, 310
Bettel, W., new colour test for molybdenum, 40
note on the purification of mercury, 158
tellurium, 169
Bevan, E. J., J. F. Briggs, and C. F. Cross. (*See* Cross, C. F.)
Biltz, H., and L. Gonder, niobium sulphide, 50
W., and F. Zimmermann, action of silver nitrate and mercuric nitrate upon some inorganic hydroxides, 60
"Biochemistry, Descriptive" (review), 82
Bismuth, determinations of small quantities, 45
electrolytic deposition, 36
pentavalent, 133
ion, existence of a bivalent in aqueous solution, 176
selenide compounds of silver selenide with, 288
Blaise, E. E., constitution of β-acetoxy-ketones, 46
and I. Herman, β-αα-dialcoholated ketone alcohols, 250
syntheses by mixed organometallic compounds of zinc, 179
Blanc, G., synthesis of β-campholene lactone, 119
and L. Bouveault. (*See* Bouveault, L.)
Bloch, E., ionisation of the air by ultra-violet light, 275
Blumberg, P., and O. Diels. (*See* Diels, O.)
Boirac, E., "La Psychologie Inconnue" (review), 228
Bokman, G., and J. Sand. (*See* Sand, J.)
Bolduan, C. F., "Immune Sera" (review), 156
Bomb calorimeter, Mahler, 84
Bone, W. A., explosive combustion, with special reference to that of hydrocarbons, 196, 212
Borax, action of sulphosalicylic acid on, 179
Bordas, F., detection of helium in minerals containing uranium, 275
Borneol, 251
Bossuet, R., and P. Lebeau. (*See* Lebeau, P.)
Boudouard, O., extraction of gases contained in metals, 46
Bougault, J., action of nascent hypoiodous acid upon acids of formula $R-CH=CH-CH_2-CO_2H$, 119, 179
comparative study of the dehydration of atrolactic and *p*-methoxyatrolactic acids, 263
fixation of hydrocyanic acid by benzoyl acrylic acid, 276
Bourion, F., determination of tungstic acid and its separation from other substances by a mixture of chlorine and sulphur chloride 299
Bourquelot, E., and H. Hérissey, arbutine and some of its derivatives, 263
Bousfield, W. R., new form of pyknometer, 165
Bouveault, L., and G. Blanc, new derivatives of camphenylone, 142
and M. Levallois, formula of fenone, 132
and R. Locquin, syntheses by means of methyl and ethyl adipates, 95, 119
synthesis of racemic dihydrocamphoric acid, 117
Bouyssy, M., and H. Henriet. (*See* Henriet, H.)
Bouzat, M., ammoniacal cuprous sulphate, 119
Boyd, D. R., and E. R. Marle, condensation of epichlorhydrin with phenols, 236
Bragg, W. H., and J. P. V. Madsen, experimental investigation of the nature of γ-rays, 162
Brazilein, 308
Brazilin and hæmatoxylin, 129
and their derivatives, 308
Briggs, J. F., E. J. Bevan, and C. F. Cross. (*See* Cross, C. F.)
S. H. C., constitution of coordinated compounds, 236
Briner, E., and E. Durand, formation of ozone by the silent discharge at a low temperature, 46
Bristol, Merchant Venturers' Technical College, 284
British Association, Dublin Meeting, 96
Winnipeg Meeting, 144
"British Journal Photographic Almanac" (review), 83
"British Minerals and Where to Find Them" (review), 178
Brochet, A., radio-activity of Plombieres waters, 132
Bromates of the rare earths, 61
Bromide, mercuric, action of gaseous PH_3 on, 35
Bromide-bromate mixture and potassium-aluminium sulphate, reaction between, 102
Bromides, test for, alone or in solution with chlorides, 307
Bromination of *p*-hydroxydiphenylamine, 92
Bromine, action on dithymol, 143
wandering of in transformation of nitroaminobromobenzenes, 154
cyanide and cyanamide derivatives, preparation, 168
Bromo-acetates, rate of hydrolysis by water and by alkali, 235
Bromonitrophenols, 166
Browne, A. W., and F. F. Shetterly, oxidation of hydrazine, 54, 63
Bruce, E. M., "Detection of the common Food Adulterants" (review), 191
Bruneau, P., and G. Bertrand. (*See* Bertrand, G.)
Brunel, L., ketone derived from β-hexahydrocarvacrol, 59
Bryan, G. H., note on certain dynamical analogues of temperature equilibrium, 156
Bucherer, H. T., and J. Schenkel, reactions of pyridine, 312
Bugge, G., and K. A. Hofmann. (*See* Hofmann, K. A.)
Buisson, H., and C. Fabry. (*See* Fabry, C.)
Bulow, C., and E. Klemann, amido-group attached to the nitrogen atom of heterocyclic compounds, 48
Burger, O., and K. A. Hofmann. (*See* Hofmann, K. A.)
Burgess, G. K., melting-points of the iron group elements by a new radiation method, 28
Burke, Katharine A., "Thermochemistry" (review). 239
Burrows, H., and C. A. Keane, autolysator, 286
Burton, C. V., modified theory of gravitation, 248
Butcher, Miss D. D., experiments on artificial fulgurites, 225
Butter, determination of cocoanut oil in, 146
estimation of cocoanut oil in, 110

CABLES, apparatus for demonstrating propagation of alternate current waves in, 189
examination of the formulæ for the grading of, 249
Cadmium, electrolytic deposition, 137, 149
ion, existence of a univalent in aqueous solution, 176
Caille, H., and G. Perrier. (*See* Perrier, G.)
Cain, J. C., "Chemistry of the Diazo-compounds" (review), 228
note on the oxidation of phenylhydrazine by Caro's acid, 177
para- and meta-nitrosoacetanilide, 177
Calcium, metallic, action on alcohols, 10
on ketones, 11
carbide and acetylene, synthesis, 167
cyanamide production, utilisation of atmospheric nitrogen in, 289, 303
oxide, heat of formation of anhydrous, 142
Calculations, reform of chemical and physical, 301
Cameron, A. T., and Sir W. Ramsay, chemical action of radium emanation, 273
lithium in radio-active minerals, 179
Campbell, N. P., and H. Hartley. (*See* Hartley, H.)
and R. H. Poole. (*See* Hartley, H.)
Camphane series, studies in, 63
Camphenylone derivatives, 142
Campholene lactone, β-, synthesis of, 119
Camphor, absorption spectrum, 261
Candle material, conversion of oleic acid into, 238
Carbohydrates, determining molecular weight of, 143
Carbon and aluminium powder, interaction, 219, 233, 238
barium carbonate, and nitrogen, influence of addition of chloride to reaction between, 87
molecule, constitution, 37
study of, 273
graphitic, in cast-irons, 35
dioxide, apparatus for automatic examination of, 286
in air, causes of variations, 288
disulphide in benzene, determination, 119
sub-oxide, 96, 311
refractometer proof of composition of, 192

Carbon tetrachloride, 312
Carbonates, action on tetrathionates, 144
of alkalis and alkaline earths, neutral, 228
Carhart, H. S., revisions of the theory of electrolysis, 140, 151, 160
Carnegie, Andrew, Research Scholarship, 24
Catalytic power of silica and alumina, 119
Catechol derivatives, action of thionyl chloride on the methylene ethers of, 153
Cederholm, Anna M., W. H. Walker, and L. N. Bent. (*See* Walker, W. H.)
Cellulose, simple and mixed esters of, 237
Central Technical College, 276
Cerium, 206
Charabot, E., and G. Laloue, essence of Magnolia kobus, 132
of Tetranthera polyantha, var. citrate nees, 167
Charcoal and liquid air, 4, 16
Charpy, G., graphite and graphitic carbon in cast-irons, 35
solubility of graphite in iron, 45
Chatiaway, F. D., depositing copper upon glass from aqueous solutions in a thin brilliantly reflecting film, 19
new general method of preparing diazonium bromides, 236
oxidation of aromatic hydrazines by metallic oxides, permanganates, and chromates, 69
quantitative conversion of aromatic hydrazines into diazonium salts, 176
Chauvenet, E., thorium oxyfluoride and fluoride, 288
Chelsea, South-Western Polytechnic, 72, 124
"Chemical Appointments, Official" (review). 237
Chemical and physical calculations, reform of, 301
change, determination of rate of by measurement of gases evolved, 93
constitution and dielectric constant, relation between, 262
Laboratory Fresenius at Wiesbaden, 192
plant, some modern, 286
Society, 8, 67, 81, 91, 126, 153, 165, 176, 234, 246, 259, 272, 306
annual general meeting, 223
research fund, 251
transformation, change of weight in, 1
"Chemistry, Leather Trades" (review), 287
"Chemistry of the Diazo-compounds" (review), 228
"Chemistry of Gas Manufacture" (review), 95
"Chemistry, Treatise on" (review), 178
"Chemistry, Analytical, Systematic Introduction to" (review), 287
"Chemistry, Analytical, Treatise on Qualitative" (review), 46
"Chemistry, Organic, Short Textbook of" (review), 250
"Chemistry, Organic, Text-book of" (review), 71
"Chemistry, Practical, Valentin's" (review), 95
Chemistry, biological, examination, 96, 103
technical, in Russia, 238
Chesneau, G., variations in the composition of ammonium phosphomolybdate, 263
Cheveneau, C., influence of temperature upon the optical properties of dissolved substances, 47
Chick, Frances, and N. T. M. Wilsmore, acetylketen 247
some reactions of keten, 177
Chloride, influence of addition of to reaction between barium carbonate, carbon, and nitrogen, 87
mercuric, action of gaseous PH_3 on, 35
Chlorine, action on dithymol, 239
atomic weight, 135, 146, 159
Chloroacetates, rate of hydrolysis by water and by alkali, 235
Chlorocodon, isomeride of vanillin in root of a species of, 154
a-Chlorohydrin, rate of hydrolysis by water and by alkali, 235
Chlorphosphamide, action of ammonia on, 310
Cholesterol, action of fused potassium hydroxide and hydrogen peroxide on, 261
Chree, C., address to the Physical Society, 107
Chromium sulphate, 47
Cider, detection of tartaric acid in, 47
Clack, B. W., coefficient of diffusion, 285
Clarke, F. W., composition of the red clay, 185
Claus-Chance sulphur process, waste gases of, 85
Clay, red, composition, 185
Clayton, A., residual affinity of the coumarins and thiocoumarins as shown by their additive compounds, 92
Clough, G. W., and A. McKenzie. (*See* McKenzie, A.)
"Coal" (review), 45
"Coal-tar, Industrial Products of and their Applications" (review), 203
Cobaltamine compounds, 8
Cocks, porous materials to replace in working with gases, 60
Cocoanut oil, determination in butter, 146
estimation in butter, 110
Cœrulignone, constitution, 11
Cohen, B. S., production of small variable frequency alternating currents suitable for telephonic and other measurements, 285
J. B., and W. E. Cross, use of pyridine bases as halogen carriers, 82
Collier, W. H., and H. R. Ellis. (*See* Ellis, H. R.)
Colour, murexide as a printing, 191
Colson, A., causes of the allotropic transformation of yellow phosphorus dissolved in essence of terebenthene, 179
non-existence of a common solvent for yellow and red phosphorus, 35
semi-catalysis, oxidation of hydrocarbons in presence of phosphorus, 264
transformation of solutions of yellow phosphorus into red phosphorus, 118
Columbium sulphide, 50
Combustion, explosive, 196, 212
heat of, 120, 132
of gases by incandescence, 263
without a flame, 228
Compounds, constitution of co-ordinated, 236
having simple molecular structure, optical activity of, 247
cyclic, in geranic series, mechanism of formation of, 310
optically active, influence of solvents on rotation of, 262
organic, determination of halogens in chloro-brominated, 275
Conductor, electric, action of incandescent upon surrounding gases, 34
Constant, dielectric, and chemical constitution, relation between, 262
Constants, affinity, as determined by aid of methyl-orange, 127
dissociation, of triazoacetic and *a*-triazopropionic acids, 259
Constants, thermo-chemical, calculation of, 183, 253, 266
Contact potential differences determined by means of null solutions, 129
Cooke, W. T., E. H. Rennie, and A. J. Higgin. (*See* Rennie, E. H.
Copper and Brass Institute, 108
alloys, determination of small percentages of iron in, 10
and nitric acid, interaction in presence of metallic nitrates, 306
depositing upon glass from aqueous solutions in a thin brilliantly reflecting film, 19
electrolytic deposition, 137, 149
influence on fermentation, 79, 87
in complicated organic salts, determination, 192
iodometric determination, 174, 187
precipitation as metal by titanium sesquisulphate, 168
glycocoll sulphates, physico-chemical study of the complex, 11, 37, 51
mirror, producing, 19
Corrosion of iron and steel, 31, 40
Cotton, characterisation of mercerised, 10
Coumarins and thiocoumarins, residual affinity of, 92
Couriot, M., and J. Meunier, action of incandescent electric conductor upon surrounding gases, 34
Cousin, H., action of chlorine on dithymol, 239
and H. Hérissey, preparation of dithymol, 143
Crookes, Sir W., scandium, 258
Cross, C. F., E. J. Bevan, and J. F. Briggs, chloramic reactions of the proteins, 131
W. E., and J. B. Cohen (*See* Cohen, J. B.)
Crossley, A. W., and C. Gilling, hydroaromatic ketones, 272
and Nora Renouf, nitro-derivatives of *o*-xylene, 153
substituted dihydrobenzenes, 153
Crystallisation, spontaneous, of substances which form a continuous series of mixed crystals, 263
Cumming, A. C., malacone, a silicate of zirconium, 93
Cupric salts, colour of in aqueous solution, 10
Curie, Mdme, condensation of water vapour in presence of radium emanation, 35
Currents, alternating, production of small variable frequency, 285
Cyprus origanum oil, constituents, 235

"DAIRY Laboratory Guide" (review), 191
Damm, F., and F. Krafft, autoreduction of some metallic oxides in the cathode light vacuum, and volatility of the corresponding sulphides, 43
Darzens, G., glycide ethers and aldehydes in the naphthalene series, 47
and H. Rost, new method of preparing the homologues of naphthalene, 276
Davy, discovery of the alkali metals by, 11, 193, 210
Dawson, H. M., and C. G. Jackson, influence of foreign substances on certain transition temperatures and the determination of molecular weights, 92
D'Ans, J., ammonium syngenite, 143
and W. Zeh, rubidium calcium sulphates, 60
De Forcrand, M., action of heat on the hydrates of lithium hydroxide, 264
heat of formation of anhydrous oxides of lithium, calcium, strontium, and barium, 142
neutral carbonates of alkalis and alkaline earths, 228
De Gramont, apparatus for producing the spark spectra of solutions, 35
De Vulitch, V., "Les Produits Industriels des Goudrons de Houilles et leurs Applications" (review), 203
Dean, G. W., determination of silica and alumina in iron ores, 31
Decker, H., and G. Dunant, "Guide de Preparations Organiques" (review), 45
Deinhardt, K., and A. Schlomann, "Technical Dictionary" (review), 178
Delaunay, N., certain relations between the atomic weights of elements, 46
symmetry in the law of atomic weights, 99
Delépine, M., properties of metallic thiosulphocarbamates, 288
Deming, C. D., and I. K. Phelps. (*See* Phelps, I. K.)
Denham, H. G., existence in aqueous solutions of a univalent cadmium ion, a subvalent thallium ion, and a bivalent bismuth ion, 176
and A. J. Allmand, anomalous behaviour of the hydrogen electrode in solutions of lead salts, and existence of univalent lead ions in aqueous solutions, 81
Dennis, L. M., and Ellen S. McCarthy, determination of benzene in illuminating gas, 282, 293
Des Bancels, J. L., physical modifications of gelatin in presence of electrolytes and non-electrolytes, 143
Desch, C. H., and A. K. Huntington. (*See* Huntington, A. K.)
Dewar, Sir J., Albert Medal, 312
solidification of helium, 121, 200
studies on charcoal and liquid air, 4, 16
Diamond, conversion into coke in high vacuum by cathode rays, 170
"Diazo-compounds, Chemistry of" (review), 228
Diazomethane, action on two modifications of iso-nitrosocamphor, 68
and mercuric acetate, action of, 166
Diazonium bromides, preparing, 236
salts, converaion of aromatic hydrazines into, 176
reaction with mono- and dihydric phenols and with naphthols, 260
Diazo-reaction in diphenyl series, 128
Dibenzoylbenzene, *o*-, amide derivatives of, 288
Dibenzyl diselenide, 273
Dibenzylsilicone, 92
"Dictionary, Technical" (review), 178
Didymium salts, variations of absorption bands of in a magnetic field, 49
Diels, O., and P. Blumberg, carbon suboxide, 96, 311
Diffusion, coefficient of, 285
Dihydrobenzenes, substituted, 153
Dihydromyrcene, synthesis and structure, 310
Dimercurammonium chlorides, ammoniacal, 263
Dimethylanthracene, 1.6 and 2.7, simultaneous production, 119, 152

Dimethylsulphate, action on alkaline polysulphides, 311
Dinaphthacridine, β—N—β / β—CHβ -, attempted synthesis, 8
Diones, aromatic, direct hydrogenation, 34
Diphenyl series, diazo-reaction in, 128
Diphenylcamphomethane, isomer of, 263
Diselenides, preparation, 273
"Disinfectants, Survey of the German Patents dealing with Remedies and" (review), 239
Distillation, vacuum, manometer for, 128
Dithymol, action of bromine on, 143
of chlorine on, 239
preparation, 143
Divers, E., action between potassium sulphite and potassium pentathionate, 262
decomposition of hyponitrous acid, 82
Dixon, A. E., and J. Taylor, constitution of thiocyanates containing an electronegative group, 176
Dolomite, decomposition, 217
Drushel, W. A., volumetric estimation of lanthanum as the oxalate, 111
of potassium as the cobaltinitrite, 124
Drysdale, C. V., dynamometer wattmeters, 190
notes on the plug permeameter, 189
use of shunts and transformers with alternate current measuring instruments, 189
vacuum tube apparatus, 189
Duboin, A., iodomercurates of thorium and aluminium, 258
sulphur compounds of thorium, 264
Duddell, W., short spark phenomena, 225
Dunant, G., and H. Decker. (*See* Decker, H.)
Dunstan, A. E., and F. B. T. Thole, viscosity of aqueous pyridine solutions, 153
and G. Young. (*See* Young, G.)
W. R., mercuric zinc cyanide, 274
Duparc, L., and A. Monnier, "Traite de Chimie Analytique Qualitative" (review), 46
Dupuis, P., and V. Auger. (*See* Auger, V.)
Durand, E., and E. Briner. (*See* Briner, E.)
Düriog, E. A. F., "Übersicht uber die Deutschen Reichpatente betreffend Heilmittel und Desinsektionsmittel" (review), 239
Duval H., reciprocal displacement of hydrocarbon groups in Friedel and Craft's reaction, 167
Dyeing, theory of, 130
Dyer, B., "Fertilisers and Feeding Stuffs" (review), 202
Dyes, acid and basic, dissociation of compounds of by adsorbent substances, 35
influence of acids and bases on fixation of by wool, 47
iso-cyanine, optical and sensitising properties of, 274
orthobenzylated, from triphenylmethane, 299
Dye-stuff, murexide as a quondam, 191
Dynamometer wattmeters, 190
Dysprosium, 208
and terbium, compounds of, 75
ultra-violet spark spectrum and magnetic properties of, 277

EARTHS, alkaline, and alkalis, neutral carbonates of, 228
rare, abnormal mobility of ions of, 132
bromates of, 61
salts, absorption spectra of crystals of, 239
separation of, 205
yttrium, 278
separation, 61
Echeandia, E., A. Stock, and P. R. Voigt. (*See* Stock, A.)
Eddy, E. A., and F. A. Gooch. (*See* Gooch, F. A.)
Edgar, G., determination of vanadic and molybdic acids in presence of one another, 245
"Education of To-morrow" (review), 178
Electric fields, distribution in of active deposits of radium, thorium, and actinium, 156
Electrolysis, theory of, 140, 151 160
Electrons, phenomena in spark spectrum of yttrium attributable to, 250
Electro-syntheses, 48
Elements, non-metallic in connection with valency and specific gravity, 265
atomic weights of, relations between, 46
potential energy of, 302
chemical, periodicity, weight, and valency, 122
iron group, melting-points, 28
Ellis, H. R., and W. H. Collier, oxidation of ferrous hydrate by cupric hydrate in the presence of ammonia, 121
and F. E. Weston. (*See* Weston, F. E.)
Engels, P., W. H. Perkin, jun., and R. Robinson, brazilin, hæmatoxylin, and their derivatives, 308
"English Electro-chemical Patents" (review), 192
Epichlorohydrin, condensation with phenols, 236
Erbium, 209
salts, variations of absorption bands of in a magnetic field, 49
Errera, L., "Cours de Physiologie Moléculaire (review), 83
Essence of Magnolia kobus, 132
of Tetranthera polyantha, var. citrate nees, 167
Ester hydrolysis, 309
acetic, bistriazo-derivatives of 248
propionic, azoimides of, 129
Esterification of succinic acid, 112
theories of, 309
Esters, formation and hydrolysis, of, 310
of arsenious acid, 309
Ethane, bistriazo-derivatives of, 248
Ether of apace, 255, 269
Ethers, phenolic, sulphination of 154
Ethyl and methyl adipates, syntheses by means of, 95, 119
cyanide, preparation, 47
esters of malonic and cyanoacetic acids, action of mustard oils on, 129
formate, saponification of, 248
6-methyl-2-pyrone-3 : 5-dicarboxylate and derivativea, 274
tartrate in aromatic halogen derivativea, 262
Europium, 208
atomic weight, 173
Evans, C. de B., traces of a new tin-group element in thorianite, 154
Everatt, R. W., effect of constitution on optical activity of nitrogen compounds, 308
and K. J. P. Orton. (*See* Orton, K. J. P.)
Ewins, A. J., and G. Barger. (*See* Barger, G.)
Examination, biological chemistry, 96, 108
Exhibition, Infants' Health, 276
Explosions, 286
Explosive combustion, 196, 212
works, buildings of, 286

FABRY, C. and H. Buisson, presence of spark lines in the arc spectrum, 263
Faraday Society, 11, 126, 131, 238, 274
"Fats and Oils, Technology of" (review), 179
Fawsitt, C. E., viscosity determinations at high temperatures, 308
of solutions, 261
Feeding stuffs, cyanogenetic glucosides in, 191
"Feeding Stuffs, Fertilisers and" (review), 202
Fehling's solution, keeping power and determining reducing sugars with it, 45
Fenchone and *a*-methylcamphor, 309
Fenone, formula of, 132
Fenton, H. J. H., titani-dihydroxymaleic acid and the detection of titanium, 273
Ferchland, P., "Die Englischen Elektrochemischen Patente" (review), 192
Fermentation, influence of light and of copper on, 79, 87
of mannose and lævulose by yeast juice, 259
studies in, 69
alcoholic, mechanism of, 69
Ferropyrophosphatea, reducing power of, 264
"Fertilisers and Feeding Stuffs" (review), 202
Fertilising value of snow, 243
Fierz, H. E., and M. O. Forster. (*See* Forster, M. O.)
and W. P. Joshua. (*See* Forster, M. O.)
Filtration, mechanism of, 238
Fischer, E., "Guide de Preparations Organiques" (review), 45
F., and O. Ringe, formation of hydrogen peroxide, 251
Fitzgerald, E., and A. Lapworth, experiments on the formation and hydrolysis of esters, acetals, and allied compounds, 310
Flaschner, O., and B. MacEwen, mutual solubility of 2-methylpiperidine and water, 261
Flours, wheat, considerations affecting atrength of, 190
"Food Adulterants, Detection of the Common" (review), 191
Formamide, preparation from ethyl formate and ammonium hydroxide, 86
Forster, M O., and H. E. Fierz, triazo-group, 129, 306
and W. P. Joshua, triazo-group, 248
and H. Holmes, studies in the camphane series, 68
Fosse, R., constitution of compounds of tetramethyldiaminobenzhydrol with some methylenic derivatives, 299
new reactions of aromatic alcohols, 47
Fourneau and Tiffeneau, MM., styroline oxide, 250
Fox, J. J., and J. T. Hewitt. (*See* Hewitt, J. T.)
Frank, A., utilisation of the atmospheric nitrogen in the production of calcium cyanamide, 289, 303
Frankel, S., "Deacriptive Biochemie" (review), 83
Friedel and Craft's reaction, formation of mixtures of isomers of constant melting-point in, 263
reciprocal displacement of hydrocarbon groups in, 167
Friend, J. A. N., criticism of Werner s theory, and constitution of complex salts, 262
Friend, J. A. N., history of valency, 171
valency, 81
Frion, P., carrying down of soluble substances by certain precipitates, 275
Friswell, R. J, preparation of para-toluidine from mixed toluidines by means of para-toluidine hydrate, 131
Fulgurites, artificial, 225

GADOLINIUM, 208
fluoride, 157
Gaillard, G., time taken by substances to dissolve, 298
Gain, G., isomeric modification of hydrated hypovanadic acid, 179
Garry, H. S., "Process Cost Accounts" (review), 287
"Gas Manufacture, Chemistry of" (review), 95
"Gas, Town, and its Uses" (review), 34
"Gas Reactions, Thermodynamics of Technical" (review), 287
Gas burettes, combined stopcock and capillary connecting tube for, 237
determination of benzene in illuminating, 282, 293
Gaudechon, H., ammoniacal chlorides of dimercurammonium, 263
dissociation of double chlorides of dimercuric ammonium and ammonium by water, 132
Gasea, action of incandescent electric conductor upon surrounding, 34
combustion by incandescence, 263
ignition at end of strip of metal, 228
in metals, extraction of, 46
occluded in steel, 46
porous materials to replace cocks in working with, 60
waste, of Claus-Chance sulphur process, 85
Gebhard, N. L., simple manometer for vacuum distillation, 128
Gelatin, physical modifications in presence of electrolytes and non-electrolytes, 143
Geranic series, mechanism of formation of cyclic compounds in, 310
"German Patents dealing with Remedies and Disinfectants" (review), 239
Gerum, J., and C. Paal. (*See* Paal, C.)
Geyer, A., and W. Autenrieth. (*See* Autenrieth, W.)
Gibbs' theory of surface concentration, 130
Giesel, F., preparation and behaviour of polonium, 242, 277
Gilling, C., and A. W. Crossley. (*See* Crossley, A. W.)
Gilman, A. F., "Laboratory Outline for Determinations in Quantitative Chemical Analysis" (review), 297
Gittins, J. M., and J. J. Sudborough. (*See* Sudborough, J. J.)
Glass, depositing copper upon from aqueous solutions in a thin brilliantly reflecting film, 19
Glassmann, B., constitution of fatty acid salts of beryllium, 95
Gleditsch, Mdlle., lithium in radioactive minerals, 167
Glover, W. H., *a*-methylcamphor and fenchone, 309
Glucinum, constitution of fatty acid salts of, 95
Glucosides, cyanogenetic, in feeding stuffs, 191
Glycerin nitrates, 311
Glycide ethers and aldehydes in naphthalene series, 47

Glycols, aromatic, mechanism of phenyl transpositions in, 72
Godchot, M., and E. Jungfleisch. (*See* Jungfleisch, E.)
Godden, W., condensation products from aminopinenedicarboxylic acid, 307
Gonder, L., and H. Biltz, niobium sulphide, 50
Gooch, F. A., and E. A. Eddy, separation of magnesium from the alkalis by alcoholic ammonium carbonate, 280
and F. H. Heath, iodometric determination of copper, 174, 187
and R. W. Osborne, reaction between potassium-aluminium sulphate and a bromide-bromate mixture, 102
Gortner, R. A., W. R. Lang, and J. F. Mackey. (*See* Lang, W. R.)
Gouère, M., rapid determination of potassium bichromate in milk, 143
Goulding, E., and R. G. Pelly, new isomeride of vanillin occurring in the root of a species of chlorocodon, 154
volatile oil of the leaves of Ocimum viride, 154
Graphite, density of, 98
in cast-irons, 35
solubility in iron, 45
Gravitation, modified theory of, 248
Gregory, A. W., colorimetric method for the determination of small percentages of iron in copper alloys, 10
new test for silver, 262
Grignard, V., and P. Barbier. (*See* Barbier, P.)
Gross, T., decomposition of platinum by an alternating current, 62
Groves, C. E., cobaltamine compounds, 9
Guaiacol, phosphoric acid ethers of, 310
Guerbet, M., action of alcohols on sodium benzylate, 143
transformation of *a*-oxyacids into aldehydes by boiling an aqueous solution of their mercuric salts, 119
Guillet, L., constitution of manganese cast irons, 118
Gustavson, G., products of the action of aluminium chloride and hydrochloric acid on benzene, 239
Gutbier, A., and A. Hüttlinger, rhodium, 143
Gutmann, A., action of carbonates on tetrathionates, 144
Guttmann, O., explosions, and the building of explosive works, 286
some modern chemical plant, 286
Guyot, A., and P. Pignet, ortho-benzylated dyes from triphenylmethane, 299
and P. Piquet, amide derivatives of *o*-dibenzoylbenzene, 288

HABER, F., "Thermodynamics of Technical Gas-reactions" (review), 287
Hackspill, L., alloys of platinum and thallium, 264
Hæmatein, 308
Hæmatoxylin and brazilin, 129
and their derivatives, 308
Haller, A., alcoholysis of linseed oil, 142
and E. Bauer, isomer of diphenylcamphomethane, 263
Halogen carriers, use of pyridine bases as, 82
derivatives, ethyl tartrate in aromatic, 262
of open-chain hydrocarbons, crystal form of with reference to Barlow-Pope theory of structure, 93
Halogen displacement in 1-phenylchloroacetic acid by hydroxy and methoxy groups, 235
Halogens in chloro-brominated organic compounds, 275
Hancu, V., and J. Herzog. (*See* Herzog, J.)
Hanneke, P., "Photographisches Rezept-Taschenbuch" (review), 46
Hanssen, C. J. T., reform of chemical and physical calculations, 301
Hantzsch, A., and J. Oechslin, metacetaldehyde, 8
Harden, A., and W. J. Young, fermentation of mannose and lævulose by yeast juice, 259
Harries, C., action of ozone upon substances containing a triple bond, 59
lecture experiments with ozone, 89
Hartley, H., and N. P. Campbell, solubility of iodine in water, 153
and R. H. Poole, preparation of conductivity water, 127
B. M. Jones, and G. A. Hutchinson, spontaneous crystallisation of sodium sulphite solutions, 166
N. G. Thomas, and M. P. Applebey, physico-chemical properties of mixtures of pyridine and water, 91
W. N., absorption spectra of the vapours of benzene and its homologues at different temperatures and pressures, and likewise of solutions of benzene, 97
absorption spectrum of camphor, 261
nature of the impurity found in preparations of triphenylmethane, 236
Hatschek, E., mechanism of filtration, 238
Haworth, W. N., and W. H. Perkin, jun., experiments on the synthesis of the terpenes, 155
Heat, action on hydrates of lithium hydroxide, 264
a-hydroxycarboxylic acids, 165
decomposition of ammonium dichromate by, 92
effects on alkyl iodides, 10
slow decomposition of ammonium chromate, dichromate, and trichromate by, 274
Heath, F. H., and F. A. Gooch. (*See* Gooch, F. A.)
Heess, J. K., "Practical Methods for the Iron and Steel Works Chemist" (review), 297
Hefter, G., "Technologie der Fette und Öle" (review), 179
Heilbron, I. M., and G. G. Henderson. (*See* Henderson, G. G.)
Helium in minerals containing uranium, detection, 275
solidification of, 121, 200
vacuum tubes, 95
Henderson, G. G., and I. M. Heilbron, contributions to the chemistry of the terpenes, 93
Henriet, H., and M. Bouyssy, origin of ozone in the atmosphere, 288
volumetric method of determining simultaneously the carbonic acid and other acids in atmospheric air, 299
Henry, L., action of nitrous acid upon allylamine, 46
T. A., and S. J. M. Auld, occurrence of cyanogenetic glucosides in feeding stuffs, 191
Hérissey, H., and E. Bourquelot, (*See* Bourquelot, E.)
and H. Cousin. (*See* Cousin, H.)
Herman, I., and E. E. Blaise. (*See* Blaise, E. E.)
Herzog, J., and V. Hancu, quantitative determination of phenol-hydroxyl groups, 180
Heterocyclic compounds, amido-group attached to the nitrogen atom of, 48
Hewitt, J. T., and J. J. Fox, colour and constitution of azo-compounds, 67
Hexahydrocarvacrol, *β*-, ketone derived from, 59
Higgin, A. J., E. H. Rennie, and W. T. Cooke. (*See* Rennie, E. H.)
Hilditch, T. P., relation between unsaturation and optical activity, 154
and S. Smiles. (*See* Smiles, S.)
Hill, A. E., combined stopcock and capillary connecting tube for gas burettes, 237
J. R., and H. O. Jones. (*See* Jones, H. O.)
Hodgkinson, W. R., "Valentin's Practical Chemistry" (review), 95
Hofmann, K. A., and G. Bugge, platinum blue, 144
and O. Burger, neo-erbium, 145
and H. Wagner, reactions of mercury cyanide, 144
Holleman, A. F., "Text-book of Organic Chemistry" (review), 71
Holley, C. D., and E. F. Ladd, "Analysis of Mixed Paints, Colour Pigments, and Varnishes" (review), 287
Holmes, H., and M. O. Forster. (*See* Forster, M. O.)
Holmium, 208
Homberger, A. W., and V. Lenher. (*See* Lenher, V.)
Homer, Annie, and J. E. Purvis, study of the absorption spectra of the hydrocarbons isolated from the products of the action of aluminium chloride on naphthalene, 308
Hooton, W. M., decomposition of ammonium dichromate by heat, 92
Howard, G. M., determination of antimony and arsenic in lead-antimony alloys, 271
Hübner, J., characterisation of mercerised cotton, 10
Hulton, H. F. E., and J. L. Baker. (*See* Baker, J. L.)
Huntington, A. K., and C. H. Desch, planimetric analysis of alloys, and the structure of phosphor-copper, 238
Hutchins, E. B., jun., and V. Lenher, pentavalent bismuth, 133
Hutchinson, G. A., H. Hartley, and B. M. Jones. (*See* Hartley, H.)
Hüttlinger, A., and A. Gutbier. (*See* Gutbier, A.)
Hydrate, ferrous, oxidation of, 121
Hydrated salts, use of vacuum for drying, 48
Hydrates of arsenic acid, 239
of fatty acids, 310
Hydrazine oxidation, 54, 63
Hydrazines, aromatic, conversion into diazonium salts, 176
oxidation, 69
Hydrindene, formation of derivatives of from *o*-phenylenediacetonitrile, 81
Hydrocarbon groups, reciprocal displacement in Friedel and Craft's reaction, 167
Hydrocarbons, crystal form of halogen derivatives of open-chain with reference to Barlow-Pope theory of structure, 93
explosive combustion with special reference to, 196, 212
isolated from products of action of aluminium chloride on naphthalene, absorption spectra of, 308
oxidation in presence of phosphorus, 264
Hydrogen and platinum, reduction with, 312
Hydrogen, anomalous behaviour of in solutions of lead salts, 81
atomic weight, 56, 58, 64, 76
peroxide, formation, 251
Hydrogenation of aromatic diones, 34
quinones, 179
Hydrolysis as illustrated by heats of neutralisation, 131
ester, 309
of amygdalin by emulsin, 246
of esters, acetals, and allied compounds, 310
Hydropiperoin, 153
Hydrosol, liquid, of palladium hydride, 192
Hydroxides, inorganic, action of silver nitrate and mercuric nitrate on, 60
metallic, amphoteric, 82
Hydroxyazo-compounds, constitution, 166
p-, salts of with mineral acids, 67
Hydroxydiphenylamine, *p*-, bromination, 92

IMINO-COMPOUNDS, formation and reactions, 81
"Immune Sera" (review), 156
"Immunochemistry" (review), 83
Indigotin and potassium permanganate, reaction between, 312
Indium and iron, separation, 217
compounds, 244
Infants' Health Exhibition, 276
"Institute of Chemical Research in the Tropics, Quarterly Journal of" (review), 228
Institute of Chemistry, annual meeting, 117
examinations, pass list, 72, 216
of Metals, 251
Intramolecular rearrangement in inactive substances, 274
Inversion, Walden, chemistry of, 235
Iodates of the alkalis and the ammonium radicle, 10
Iodide chloride, preparation, 251
Iodides, compounds of sulphur with, 218
Iodine, solubility in water, 153
Iodinium and iodo-compounds, preparation, 251
Iodohydrines, mechanism of phenyl transpositions in, 72
Ionisation of air by ultra-violet light, 275
Ionium, 75
Ions of rare earths, abnormal mobility of, 132
"Iron and Steel" (review), 250
"Iron and Steel Works Chemist, Practical Methods for" (review), 297
"Iron, Metallurgy of" (review), 287
Iron and Steel Institute, 211, 300
and indium, separation, 217
corrosion, 31, 41
estimation by potassium permanganate after reduction with titanous sulphate, 218
ferrous, determination, 122
group elements, melting-points, 28
in copper alloys, determination of small percentages, 10
in ferric compounds, volumetric estimation, 50
ores, determination of silica and alumina in, 31
solubility of graphite in, 45
salts, complex, in which the iron is masked, 142
Irons, cast, graphite and graphitic carbon in, 35
Irvine, J. C., and D. McNicoll, condensation of benzoin with methyl alcohol, 260
and Agnes M. Moodie, derivatives of tetramethyl glucose, 9
Isaac, Florence, temperature of spontaneous crystallisation of mixed solutions, and their determination by means of the index of refraction, 93
and H. A. Miers. (*See* Miers, H. A.)

Isomer of diphenylcamphomethane, 263
Isomeride of vanillin in root of a species of chlorocodon, 154
Isomers of constant melting-point in Friedel and Craft's reaction, formation, 263
Isospartеine, 47, 119
Isoxazoles, synthesis of, 311

JACKSON, C. G., and H. M. Dawson. (*See* Dawson, H. M.)
T. C., "Law of Master and Servant" (review), 95
Jaeger, F. M., crystal form of halogen derivatives of open-chain hydrocarbons with reference to the Barlow-Pope theory of structure, 93
James, C., bromates of the rare earths, 61
scheme for separation of rare earths, 205
Jamieson, J. S., delicate test for bromides alone or in solution with chlorides, 307
Jantsch, G., determination of the atomic weight of europium, 173
and G. Urbain. (*See* Urbain, G.)
Jeffreys, C. W., and F. E. Weston. (*See* Weston, F. E.)
Jet, origin of, 181
Jolibois, P., and P. Lebeau. (*See* Lebeau, P.)
Jones, B. M., H. Hartley, and G. A. Hutchinson. (*See* Hartley, H.)
H. O., and J. R. Hill, effect of constitution on rotatory power of optically active nitrogen compounds, 93
L. M., and T. S. Price. (*See* Price, T. S.)
Joshua, W. P., M. O. Forster, and H. E. Fierz. (*See* Forster, M. O.)
"Journal of the Board of Agriculture" (review), 297
Jungfleisch, E., and M. Godchot, new homologues of diglycollic acid, 72

KAHAN, Z., effect of heat on alkyl iodides, 10
Kampschulte, W., and W. Manchot. (*See* Manchot, W.)
Karl, A., triboluminescence of inorganic substances, 301
Keaoe, C. A., and H. Burrows. (*See* Burrows, H.)
Keen, W. H., volumetric method for determination of zinc, 201, 215
Keetman, B., and W. Marckwald. (*See* Marckwald, W.)
Kelvin, Lord, the late, 36, 71
Keten polymeride, 247
Ketene reactions, 177
Ketenes, 180, 192
Ketone derived from β-hexahydrocarvacrol, 59
alcohols, 179
β-αα- dialcoholated, 250
Ketones, action of metallic calcium on, 11
hydroaromatic, 272
Kinzbrunner, C., "Technical Dictionary" (review), 178
Kipping, F. S., organic derivatives of silicon, 127
and H. Marsden. (*See* Marsden, H.)
and R. Robison. (*See* Robison, R.)
Klemann, E., and C. Bulow. (*See* Bulow, C.)
Klever, H. W., and H. Staudinger. (*See* Staudinger, H.)
Knecht, E., precipitation of copper as metal by titanium sesquisulphate, 168
synthesis of calcium carbide and acetylene, 167
visible autoxidation, 167
Knight, N., decomposition of dolomite, 217
determination of ferrous iron, 122
Knox, J., study of sulphur anion and of complex sulphur anions, 131
Krafft, F., use of vacuum for drying hydrated salts, 48
and F. Damm. (*See* Damm, F.)
Krassousky, K., order of addition of ammonia to organic *a*-oxides of asymmetric structure, 142
Kühling, O., and O. Berkhold, influence of addition of chloride to reaction between barium carbonate, carbon, and nitrogen, 87

LABILE isomerism among acylsalicylamides and acyl-hydroxylamines, 177
Laby, T. H., Landolt's experiments on change of weight in chemical transformation, 1
Lactones of dihydrobrazilic and dihydrohæmatoxylinic acids, 129
Ladd, E. F., and C. D. Holley. (*See* Holley, C. D.)
Lævulose, fermentation by yeast juice, 259
Laloue, G. and E. Charabot. (*See* Charabot, E.)
Lamb, A. B., "Thermodynamics of Technical Gas-reactions" (review), 287
Lambert, B., and A. P. Walden. (*See* Walden, A. F.)
Lamplough, F. E. E., determination of rate of chemical change by measurement of the gases evolved, 93
Landolt's experiments on change of weight in chemical transformation, 1
Lang, W. R., J. F. Mackey, and R. A. Gortner, some esters of arsenious acid, 309
and J. C. Woodhouse, volumetric estimation of silver, 261
Lanthanum, 207
volumetric estimation as the oxalate, 111
Lapworth, A., ester hydrolysis and theories of esterification, 309
saponification of ethyl formate by water in presence of acids as catalytic agents, 248
and E. Barrett. (*See* Barrett, E.)
and E. Fitzgerald. (*See* Fitzgerald, E.)
Larmor, J., physical aspect of atomic theory, 109
Lavaux, J., simultaneous production of 1.6- and 2.7-dimethylanthracene, 119, 152
Law, H. D., and F. M. Perkin, action of metallic calcium on ketones, 11
"Law of Master and Servant" (review), 95
Le Chatelier, H., and S. Wologdine, density of graphite, 98
Le Pla, Margaret, and J. F. Spencer. (*See* Spencer, J. F.
Le Rossignol, S., and S. Smiles. (*See* Smiles, S.)
Le Roy, G. A., detection of tartaric acid in cider, 47
Le Sueur, H. R., action of heat on *a*-hydroxycarboxylic acids, 165
Lead in complicated organic salts, determination, 192
antimony alloys, determination of antimony and arsenic in, 271
ions, univalent, in aqueous solutions, 81
nitrate and sodium nitrate, mixtures of solutions of, 93
salts, anomalous behaviour of hydrogen electrode in solutions of, 81
"Leather Trades' Chemistry" (review), 287
Lebeau, P., and R. Bossuet, magnesium silicide, 143
and P. Jolibois, definite compounds of silicon and palladium, 299
Léger, E., transformation of barbaloin into β-barbaloin, 35
trichlorophenol, OH(1)Cl(2.4.6), and its transformation into chlorinated quinones, 250
Lemoult, P., action of gaseous PH_3 on mercuric chloride and bromide, 35
Lenher, V., yttrium earths, 278
and A. W. Homberger, gravimetric determination of tellurium, 292
and E. B. Hutchins, jun. (*See* Hutchins, E. B., jun.)
and H. B. North, action of thionyl and sulphuryl chlorides on selenium and selenium dioxide, 158
and S. Weidman. (*See* Weidman, S.)
and E. Wolesensky, selenium nitride, 174
Leonard, A. G. G., absorption spectrum of triphenylmethane, 236
Lespieau and Pariselle, MM., propargylcarbinol, 299
and M. Viguier, γ-oxytetrolic acid, 143
Letellier, M., reducing properties of organo-metallic compounds, 167
Levallois, M., and L. Bouveault. (*See* Bouveault, L.)
Lewis, W. C. M., experimental examination of Gibbs' theory of surface concentration regarded as the basis of adsorption and its application to theory of dyeing, 130
Lewkowitsch, J., conversion of oleic acid into candle material, 23
"Lichens" (review), 34
Light, influence on fermentation, 79, 87
ultra-violet, ionisation of air by, 275
reactions of, 60
Linck, G., and P. Moller, red phosphorus, 312
Lincoln, A. T., and J. H. Walton, jun., "Exercises in Elementary Quantitative Analysis" (review), 296
Linder, E., metanil yellow, 238
Linseed oil, alcoholysis of, 142
Liquids, determination of boiling-points of very small quantities, 274
organic, apparatus for determining specific inductive capacity of, 262
Lithium in radio-active minerals, 167, 179
hydroxide, action of heat on hydrates of, 264
nitrite, and its decomposition by heat, 176
oxide, heat of formation of anhydrous, 142
Llewellyn, W. G., apparatus for sublimation, 198
Lloyd, F. J., official methods of analysis, 298
S. J., constitution of gallotannic acid and of tannins, 133
Lob, W., action of silent electric discharge on damp methane, 96
Locquin, R., and L. Bouveault. (*See* Bouveault, L.)
Lodge, Sir O., ether of space, 255, 269
Losanitsch, S. M., electro-syntheses, 48
Lutecium and neo-ytterbium, 157

MAAS, J., and J. Sand. (*See* Sand, J.)
McCarthy, Ellen S., and L. M. Dennis. (*See* Dennis, L. M.)
McDonald, D. P., cutting sodium, 73
and T. S. Patterson. (*See* Patterson, T. S.)
MacEwen, B., and O. Flaschner. (*See* Flaschner, O.)
McKenzie, A., and G. W. Clough, displacement of halogen in 1-phenylchloroacetic acid by hydroxy- and methoxy-groups, 235
and H. Wren, preparation of *l*-benzoin, 92
Mackey, J. F., W. A. Lang, and R. A. Gortner. (*See* Lang, W. R.)
McMillan, A., and T. S. Patterson. (*See* Patterson, T. S.)
McNicoll, D., and J. C. Irvine. (*See* Irvine, J. C.)
Madsen, J. P. V., and W. H. Bragg. (*See* Bragg, W. H.)
Magnesium and alkalis, separation by alcoholic ammonium carbonate, 280
and aryl halides, interaction, 8
oxide, reducibility by carbon, 93
silicide, 143
Magnolia kobus, essence of, 132
Mahler bomb calorimeter, 84
Mailhe, A., and P. Sabatier. (*See* Sabatier, P.)
Maire, F., "Modern Pigments and their Vehicles" (review), 288
Makowka, O., osmium, 251
Malacone, 93
"Man and His Future" (review), 178
Manchot, W., formation of oxides of nitrogen in ozoniser, 167
and W. Kampschulte, acid properties of ozone, 72
Manganese cast-irons, constitution, 188
in water, determination, 3
Mannose, fermentation by yeast juice, 259
Manometer for vacuum distillation, 128
Marckwald, W., atomic weight of tellurium, 25
notes on Giesel's article on polonium, 277
and B. Keetman, ionium, 75
Marie, C., oxidation of platinum, 179
Marignacite, 198
Marle, E. R., and D. R. Boyd. (*See* Boyd, D. R.)
Marsden, H., and F. S. Kipping, organic derivatives of silicon, 69
"Master and Servant, Law of" (review), 95
Mathers, F. C., separation of iron from indium, 217
and C. G., Schluederberg, new compounds of indium, 244
"Matriculation Directory" (review), 178
Matter, organic, determining phosphorus in, 258
sulphur in, 167
Maurer, E., austenite, 264
Mayer, E. W., and R. Willstatter. (*See* Willstatter, R.)
Measuring instruments, alternate current, use of shunts and transformers with, 139
Meldrum, A. N., complex nitrites containing potassium and lead, 246
composition and formula of Wells' potassium-lead periodide, 247
αβ-lactonic acid from acetone and malonic acid, 94
and W. E. S. Turner, molecular complexity of amides in various solvents, 247
Melick, C. W., "Dairy Laboratory Guide" (review), 191
Melting-points of anilides, *p*-toluidides, and *a*-naphthalides of normal fatty acids, 261
Meniere, P., new method of determining mercury vapour in air, 263
"Merck's, E., 1907 Index" (review), 178
Mercury purification, 158
vapour in air, determining, 263
reactions of, 144
nitrite, molecular volume, 176

Metacetaldehyde, 8
Metals, extraction of gases contained in, 46
" Metallurgy of Iron" (review), 287
Metanil yellow, 238
Methanitrosoacetanilide, 177
Methane, action of silent electric discharge on damp, 96
mixed trihaloid derivatives, 299
Methyl and ethyl adipates, syntheses by means of, 95, 119
alcohol, condensation of benzoin with, 260
cyanide, preparation, 47
a-Methylcamphor and fenchone, 309
ether, of para-dimethylamido-ortho-benzoyl benzoic acid, action of phenyl magnesium bromide on the second, 276
ethers, of catechol derivatives, action of thionyl chloride and of phosphorus pentachloride on, 128, 153
Methylene dichloride, and 1-substituted-2-naphthylamines, condensation, 8
Methylethylketone, azoimides of, 129
Methylpiperidine, 2-, and water, mutual solubility, 261
Methylsparteine, *a*-, isomerisation of, 48
Meunier, J., combustion of gases by incandescence in presence of oxidisable and incombustible substances, 263
without a flame, and ignition of gases at end of a strip of metal, 228
and M. Couriot (*See* Couriot, M.)
Meyer, A., and A. Wahl. (*See* Wahl, A.)
Lothar, Memorial, 79
V., form of release for vapour-density apparatus of, 73
Michael, A., refractometer proof of composition of carbon suboxide, 192
Micklethwait, Frances M. G., and G. T. Morgan. (*See* Morgan, G. T.)
Middleton, E. G., electrolytic deposition of bismuth, 36
Miers, H. A., and Florence Isaac, spontaneous crystallisation of substances which form a contiouous series of mixed crystals, 263
" Milk and its Relation to Public Health" (review), 297
Milk, determination of potassium bichromate in, 143
freezing-point of, 241
Miller, O., and J. Smirnoff, reaction between indigotin and potassium permanganate, 312
" Minerals, British, and Where to Find them" (review), 178
Minerals containing uranium, detection of helium in, 275
radio-active, luthium in, 167, 179
Mitchell, A. D., and C. Smith. (*See* Smith, C.)
Moir, J., falsification of nitrocotton with mercuric chloride and its detection, 133
so-called tetrabromodiphenoquinone, and the constitution of cœrulignone, 11
Molecular weights, influence of foreign substances on determination, 92
Moller, P., and G. Linck. (*See* Linck, G.)
Molybdenum, colour test for, 40
hexathiocyanate salts of, 312
tetravalent, compounds, 24
Monnier, A., and L. Duparc. (*See* Duparc, L.)
Monoxides of alkali metals, heat of formation of, 119
Moodie, Agnes M., and J. C. Irvine. (*See* Irvine, J. C.)
Moore, C. W., and J. F. Thorpe, formation and reactions of imino-compounds, 81
Morgan, G. T., manufacture of sodium nitrite, 237
and Frances M. G. Micklethwait, derivatives of para-diazoiminobenzene, 127
diazo-reaction in the diphenyl series, 128
Morindin, 309
Moss, H., and S. W. J. Smith. (*See* Smith, S. W. J.)
Mott, O. B., and A. J. Walker. (*See* Walker, A. J.)
Moureu, C., and A. Valeur, constitution of isosparteine, 119
isomerisation of *a*-methylsparteine, 48
isnsparteine, 47
Muir, M. M. P., volumetric estimation of iron in ferric compounds, 50
Murexide as a quondam dye-stuff and printing colour, 191
Mustard oils, action on ethyl esters of malonic and cyanoacetic acids, 129

NAPHTHALENE, action of aluminium chloride on, absorption spectra of hydrocarbons isolated from products of, 308
glycide ethers and aldehydes in, 47
preparing homologues of, 276
Naphthylides, *a*-, of normal fatty acids, melting-points of, 261
Naphthalene and *β*-naphthol, mixtures of, 263
Nathan, Lieut.-Col. Sir F. L., and W. Rintoul, nitroglycerin and its manufacture, 74
Neil, J. S., " British Minerals and Where to Find them" (review), 178
Neodymium, 208
fluoride, 157
Neo-erbium, 145
Neo-ytterbium and lutecium, 157
Neumann, B., and J. Post. (*See* Post, J.)
New Zealand boned beef, 50
Newton, H. D., estimation of iron by potassium permanganate, after reduction with titanous sulphate, 218
Nickel, determination in presence of cobalt, iron, and manganese, 47
electrolytic deposition, 137, 149
rapid determination in presence of chromium, iron, and manganese, 21
Nicolardot, P., new chromium sulphate, 47
Niobium sulphide. (*See* Columbium sulphide)
Nitrate, mercuric, action on inorganic hydroxides, 60
Nitrites, complex, containing potassium and lead, 246
Nitroamines and allied substances, transformation of aromatic, and its relation to substitution in benzene derivatives, 85
Nitroaminobromobenzenes, wandering of bromine in transformation of, 154
Nitro-cotton, falsification with mercuric chloride and its detection, 133
Nitro-derivatives of o-xylene, 153
Nitrogen atom of heterocyclic compounds, amido-group attached to, 48
barium carbonate, and carbon, influence of addition of chloride to reaction between, 87
compounds, effect of constitution on optical activity of, 308
on rotatory power of optically active, 93
atmospheric, utilisation in production of calcium cyanamide, 289, 303
oxides, formation in ozoniser, 167
Nitroglycerin and its manufacture, 74
Nitrosocamphor, iso-, action of diazomethane on modifications of, 68
North, H. B., and V. Lenher. (*See* Lenher, V.)
Noyes, W. A., atomic weight of hydrogen, 56, 64, 76
choice of the most probable value for an atomic weight, 58
" Kurzes Lehrbuch der Anorganischen Chemie" (review), 250
and H. C. P. Weber, atomic weight of chlorine, 135, 146, 159

O'DOWD, L., and F. M. Perkin. (*See* Perkin, F. M.)
Obituary, W. A. Shenstone, 83
Ocimum viride, volatile oil of leaves of, 154
Oechslin, J., and A. Hantzsch. (*See* Hantzsch, A.)
Ohnes, K., solidification of helium, 121
Oil, cocoanut, in butter, determination, 146
estimation, 110
Cyprus origanum, constituents, 235
linseed, alcoholysis of, 142
volatile, of leaves of Ocimum viride, 154
" Oils, Technology of Fats and" (review), 178
Oils, mustard, action on ethyl esters of malonic and cyanoacetic acids, 129
Olive bark, constituents of, 260
leaves, constituents of, 260
Onnes, H. K., and J. Becquerel. (*See* Becquerel, J.)
Optical activity and unsaturation, relation between, 154
of compounds having simple molecular structure, 247
of nitrogen compounds, effect of constitution on, 308
properties of dissolved substances, influence of temperature on, 47
Optics, geometrical, illustrations of, 249
Orcinol in orchella weed, estimation, 286
Organo-metallic compounds, reducing properties of, 167
Origanene, 235
Orthobenzylated dyes from triphenylmethane, 299
Orthobromophenols, 166
Orton, K. J. P., and R. W. Everatt, reaction of diazonium salts with mono- and dihydric phenols and with naphthols, 260
and Constance Pearson, wandering of bromine in transformation of nitroaminobromobenzenes, 154
and Alice E. Smith, acids as accelerators in acetylation of amino-groups, 273
bromination of *p*-hydroxy-diphenylamine, 92
Osborne, R. W., and F. A. Gooch. (*See* Gooch, F. A.)
Osmium, 251
Oxidation of aromatic hydrazines, 69
of ferrous hydrate, 121
hydrazine, 54, 63
hydrocarbons in presence of phosphorus, 264
phenylhydrazine, 177
platinum, 179
phenomena produced by iodic and bromic acids, 299
products of pinene, 93
Oxides, metallic, auto-reduction in cathode light vacuum, and volatility of corresponding sulphides, 48
Oxyacids, *a*-, transformation into aldehydes, 119
Oxygen compounds, thermal constants of organic, 253
Ozone, acid properties, 72
Ozone, action on substances containing a triple bond, 59
formation, 46
in atmosphere, origin, 288
industrial uses, 275
lecture experiments with, 89
Ozoniser, formation of nitrogen oxides in, 167

PAAL, C., and J. Gerum, palladium hydride, 192
liquid hydrosol of, 192
" Paints, Colour Pigments, and Varnishes, Analysis of Mixed" (review), 287
Palladium and silicon compounds, 299
hydride, 192
liquid hydrosol of, 192
" Paper-mill Chemist" (review), 192
Paradiazoiminobenzene derivatives, 127
Paranitrosoacetanilide, 177
Paratoluidine, preparation, 131
Pariselle and Lespieau, MM. (*See* Lespieau, M.)
Parsons, C. A., and A. A. C. Swinton, conversion of diamond into coke in high vacuum by cathode rays, 170
Pascal, P., complex salts of iron in which the iron is masked, 142
new series of ammoniacal ferric salts in which the iron is masked, 142
reducing power of ferropyrophosphates, 264
" Patents, English Electro-chemical" (review), 192
Patterson, T. S., simple form of release for Victor Meyer's vapour-density apparatus, 73
and D. P. McDonald, influence of solvents on rotation of optically active compounds, 262
and A. McMillan, polarimetric study of intramolecular rearrangement in inactive substances, 274
Pearson, Constance, and K. J. P. Orton. (*See* Orton, K. J. P.)
Peaty waters, purification by freezing, 270
Pélabon, H., compounds of silver selenide with selenides of arsenic, antimony, and bismuth, 288
Pelet-Jolivet, L., dissociation of compounds of acid and basic dyes by adsorbent substances, 35
and N. Andersen, influence of acids and bases on fixation of acid and basic dyes by wool, 47
Pelly, R. G., and E. Goulding. (*See* Goulding, E.)
Peltner, E., and R. Wolffenstein. (*See* Wolffenstein, R.)
Pentamins, cobaltic, 23
Perard, J., action of phenyl magnesium bromide upon the second methyl ether of para-dimethylamido-ortho-benzoyl benzoic acid, 276
Percarbonic acid salts, 144
Periodates of alkalis and the ammonium radicle, 10
Periodic law, 226
Perkin, A. G., morindin, 309
and F. M. Perkin, electrolytic oxidation of some hydroxybenzoic acids, 308
F. M., discovery of alkali metals by Davy, 11
industrial uses of ozone, 275
and H. D. Law. (*See* Law, H. D.
and L. O'Dowd, determination of boiling-points of very small quantities of liquids, 274
and A. G. (*See* Perkin, A. G.)
and L. Pratt, action of metallic calcium on alcohols, 10

Perkin, W. H , jun., and W. N. Haworth. (*See* Haworth, W. N.)
and W. J. Pope, synthesis of 1 - methylcyclohexylidene-4 - acetic acid, 307
and R. Robinson, brazilin and hæmatoxylin, 129
and P. Engels. (*See* Engels, P.)
and M. R. Turner, synthesis and constitution of certain pyranol salts related to brazilein and hæmatein, 308
Perkin Medal, award, 144
Permeameter, plug, 189
Perrier, G., and H. Caille, formation of mixtures of isomers of constant melting-point in Friedel and Craft's reaction, 263
Peters, F., "Thermoelemente und Thermosaulen" (review), 298
PH_3, gaseous, action on mercuric chloride and bromide, 35
Phelps, I. K., and C. D. Deming, preparation of formamide from ethyl formate and ammonium hydroxide, 86
and M. A., preparation of acetamide by action of ammonium hydroxide and ethyl acetate, 104
use of zinc chloride in esterification of succinic acid, 112
Phenol-hydroxyl groups, quantitative determination, 180
Phenols and phosphorus pentachloride, reaction between, 143
condensation of epichlorhydrin with, 236
Phenyl transpositions in iodohydrines and aromatic glycols, mechanism of, 72
Phenylhydrazine, oxidation by Caro's acid, 177
Phenylisoxazolone derivatives, 240
Phenyl magnesium bromide, action on second methyl ether of para-dimethyl-amido-orthobenzoyl benzoic acid, 276
Phenylphenazothionium, *s*-, derivatives, 10
Philip, J. C., dissociation constants of triazoacetic and *a*-triazopropionic acids, 259
refraction and dispersion of triazo-compounds, 259
Phillips, H. A , and O. Silberrad. (*See* Silberrad, O.)
Phosphor-copper, structure of, 238
Phosphorus in organic matter, determining, 258
red, 312
yellow and red, non-existence of a common solvent for, 35
dissolved in essence of terebenthene, causes of allotropic transformation of, 179
transformation of solutions of into red, 118
oxybromide, 174
pentachloride, action on methylene ethers of catechol derivatives, 128
and phenols, reaction between, 143
pentasulphide, 168
Photograph, colour, a remarkable, 139
"Photographic Almanac, British Journal" (review), 83
"Photographic Guide" (review), 12
"Photographic Recipes, Pocket Book of" (review), 46
Physical and chemical calculations, reform of, 301
Society, 69, 94, 107, 129, 156, 189, 225, 248, 285
Pickard, R. H., and J. Yates, action of fused potassium hydroxide and of hydrogen peroxide on cholesterol, 261
Pickles, S. S., constituents of Cyprus origanum oil, 235
Picrates, metallic, 91
"Pigments, Colour, Analysis of Mixed Paints, Varnishes, and" (review), 287
"Pigments, Modern, and their Vehicles" (review), 288
Pignet, P., and A. Guyot. (*See* Guyot, A.)
Pilcher, R. B , biological chemistry examination, 108
"Official Chemical Appointments" (review), 297
Piltschikoff, N., technical chemistry in Russia, 238
Pinene, hydrating, 59
oxidation products, 93
Piperil, 153
Piperonyloin, 153
Piquet, P., and A. Guyot. (*See* Guyot, A.)
Platinum and hydrogen, reduction with, 312
and thallium alloys, 264
decomposition by an alternating current, 62
oxidation of, 179
blue, 144
Plombieres waters, radio-activity of, 132
Polonium, preparation and behaviour of, 242, 277
Poole, R. H., H. Hartley, and N. P. Campbell. (*See* Hartley, H.)
Pope, F. G., colour and constitution of azomethine compounds, 91
W. J., and W. H. Perkin, jun. (*See* Perkin, W. H., jun.)
and J. Read, optical activity of compounds having simple molecular structure, 247
Popovici, J., fluorides of gadolinium, neodymium, and praseodymium, 157
Porous materials to replace cocks in working with gases, 60
Post, J., and B. Neumann, "Traité Complet d'Analyse Chimique Appliquée aux Essais Industriels" (review), 71
Potassium, volumetric estimation as the cobalti-nitrite, 124
ammonium sulphate and a bromide-bromate mixture, reaction between, 102
bichromate in milk, determination, 143
hydroxide, action of fused on cholesterol, 261
lead periodide, composition and formula, 247
pentathionate and potassium sulphite, action between, 262
permanganate and indigotin, reaction between, 312
peroxide, action of fused on cholesterol, 261
sulphite and potassium pentathionate, action between, 262
Power, F. B., and F. Tutin, constituents of olive bark, 260
of olive leaves, 260
Pozzi-Escot, E., determination of nickel in presence of cobalt, iron, and manganese, 47
determining tartaric acid, 299
Praseodymium, 207
fluoride, 157
Pratt, L., and F. M. Perkin. (*See* Perkin, F. M.)
Precipitates, carrying down of soluble substances by, 275
"Preparations, Handbook of Organic" (review), 45
Price, T. S., electrolytic deposition of zinc, using rotating electrodes, 89, 99
and L. M. Jones, preparation of diselenides, 273
Propargylcarbinol, 299
Proteins, chloramin reactions of, 131
P_4S_3, P_4S_7, P_2S_5, vapour densities of, 203
"Psychology, Unknown" (review), 225
Purvis, J. E., and A. Homer. (*See* Homer, Annie)
and W. A. R. Wilks, influence of light and of copper on fermentation, 79, 87
Pyknometer, new form of, 165
Pyman, F. L., and W. C. Reynolds, aromatic arsonic and arsinic acids, 307
Pyranol salts related to brazilein and hæmatein, synthesis and constitution, 308
Pyridine and water mixtures, physico-chemical properties of, 91
bases, use as halogen carriers, 82
reactions of, 312
solutions, viscosity of aqueous, 153
Pyrogenic reactions, 11
4-Pyrone compounds, formation from acetylenic acids, 128

QUINONES, aromatic, hydrogenation, 179

RACE, J., and R. Ross. (*See* Ross, R.)
Radio-active minerals, lithium in, 167, 179
Radio-activity of Plombieres waters, 132
standard of, 33
Radio-lead, 119
Radium, atomic weight, 229
distribution in electric fields of active deposits of, 156
emanation, condensation of water-vapour in presence of, 35
emanations, initial change of, 155
chemical action of, 273
Ramsay, Sir W., and A. T. Cameron. (*See* Cameron, A. T.)
Randall, D. L., behaviour of molybdic acid in zinc reductor, 113
Rankin, D. J., potential energy of the elements, 302
I. G., and S. M. Revington. (*See* Revington, S. M.)
Ray, P. C., lithium nitrite and its decomposition by heat, 176
molecular volumes of the nitrites of silver, mercury, and the alkali metals, 176
γ-Rays, nature of, 162
Reaction between phenols and phosphorus pentachloride, 143
potassium-aluminium sulphate and a bromide-bromate mixture, 102
of diazonium salts with mono- and di-hydric phenols and with naphthols, 260
Friedel and Craft's, formation of mixtures of isomers of constant melting-point in, 263
reciprocal displacement of hydrocarbon groups in, 167
Reactions of ketene, 177
of mercury cyanide, 144
ultra-violet light, 60
pyrogenic, 11
Read, J., and W. J. Pope. (*See* Pope, W. J.)
Recalescence curves, 69
Record, F., apparatus for simultaneously extracting a solid and filtering the solution so obtained, 280
Redgrove, H. S., calculation of thermo-chemical constants, 183, 253, 266
constitution of carbon molecule from standpoint of thermochemistry, 37
Reduction with platinum and hydrogen at ordinary temperature, 312
Remington, J. S., "Education of To-morrow" (review), 178
Rengade, E., heat of solution of alkali metals and heat of formation of their monoxides, 119
Rennie, E. H., A. J. Higgin, and W. T. Cooke, interaction of copper and nitric acid in presence of metallic nitrates, 306
Renouf, Nora, and A. W. Crossley. (*See* Crossley, A. W.)
Revington, S. M., and I. G. Rankin, sulphides and oxysulphides of silicon, 272
Reynolds, H., volumetric estimation of tin by means of potassium dichromate, 13
W. C., and F. L Pyman. (*See* Pyman, F. L.)
Rhodium, 143
Rindl, M., and H. Simonis, determination of lead, copper, and silver in complicated organic salts, 192
Ringe, O., and F. Fischer. (*See* Fischer, F.)
Rintoul, W., and Lieut.-Col. Sir F. L. Nathan. (*See* Nathan, Sir F. L.)
Robertson, P. W., melting-points of the anilides, *p*-toluidides, and *a*-naphthalides of normal fatty acids, 261
orthobromophenols and some bromonitrophenols, 166
Robison, R., and F. S. Kipping, organic derivatives of silicon, 92
Robinson, R., and W. H. Perkin, jun. (*See* Perkin, W. H , jun.)
W. H. Perkin, jun., and P. Engels. (*See* Engels, P.)
and M. R. Turner. (*See* Perkin, W. H., jun.)
Roscoe, H. E , and C. Schorlemmer, "Treatise on Chemistry" (review), 178
Rosenhain, W., recalescence curves, 69
Ross, R., and J Race, estimation of cocoanut oil in butter, 110
Rosset and Besson, MM. (*See* Besson, M.)
Rost, H., and G. Darzens. (*See* Darzens, G.)
Roux, J., abnormal mobility of the ions of the rare earths, 132
Rowell, H. W., determination of small quantities of bismuth, 45
Royal Institution, 15, 48, 71, 98, 110, 120, 177, 200, 222, 226, 251, 265
Society, conversazione, 258
of Arts, 82, 192
Albert Medal of, 312
Royle, H. M., "Chemistry of Gas Manufacture" (review), 95
Rubber, valuing raw, 73
Rubidium calcium sulphates, 60
Ruhemann, S., action of mustard oils on ethyl esters of malonic and cyanoacetic acids, 129
formation of 4 - pyrone compounds from acetylenic acids, 128
Russ, S., distribution in electric fields of active deposits of radium, thorium, and actinium, 156
Russia, technical chemistry in, 238

SABATIER, P., and A. Mailhe, direct hydrogenation of aromatic diones, 34
of aromatic quinones, 179
Salts of *p*-hydroxyazo-compounds with mineral acids, 67
alkaloid, of corresponding saturated or unsaturated acids, 154
complex, constitution of, 262
ferric, ammoniacal, in which the iron is masked, 142
organic, determination of lead, copper, and silver in complicated, 192
rare earths, absorption spectra of crystals of, 239
Samarium, 208
Samarskite, 279
Sand, J., and G. Bokman, cobaltic pentamins, 23
and Johanna Maas, compounds of tetravalent molybdenum, 24
hexathiocyanate salts of molybdenum, 312

Saponification of ethyl formate, 248
Savariau, M., method of preparing cyclic aldehydes, 143
Scandium, 209, 258
Schenkel, J., and H. T. Bucherer. (*See* Bucherer, H. T.)
Schlomann, A., and K. Deinhardt. (*See* Deinhardt, K.)
Schluederberg, C. G., and F. C. Mathers. (*See* Mathers, F. C.)
Schmidlin, J., preparation of triphenylmethyl, 168
Schmidt, H., "Photographiaces Hilfsbuch" (review), 12
J., and K. T. Widmann, new synthesis of isoxazoles, 311
Schonteden, H., "Cours de Physiologie Moléculaire" (review), 83
Schorlemmer, C., and H. E. Roscoe. (*See* Roscoe, H. E.)
"Science Year Book, 1908" (review), 45
Sedgwick, W., "Man and His Future" (review), 178
Selenium and selenium dioxide, action of thionyl and sulphuryl chlorides on, 158
nitride, 174
Semicatalysis, 264
Senderens, J. B., catalytic power of silica and alumina, 119
Senier, A., and P. C. Austin, attempted synthesis of β—N—β / β—CHβ dinaphthacridine, condensation of methylene dichloride and 1-substituted-2-naphthylamines, 8
Senter, G., rate of hydrolysis of chloroacetates, bromoacetates, and α-chlorohydrin by water and by alkalis, 235
Sexton, F. P., spectrum top, 285
Shenstone, W. A. (obituary), 83
Sheppard, S. E., optical and sensitising properties of the iso-cyanine dyes, 274
Sherwood, L. T., and G. Alleman, use of tin as cathode for rapid quantitative electrolytic deposition of zinc, copper, silver, cadmium, and nickel, 137, 149
Shetterly, F. F., and A. W. Browne. (*See* Browne, A. W.)
Shutt, F. T., fertilising value of snow, 243
purification of peaty waters by freezing, 270
Sidgwick, N. V., and H. T. Tizard, colour of cupric salts in aqueous solution, 10
initial change of the radium emanations, 155
Silberrad, O., and H. A. Phillips, metallic picrates, 91
Silica in iron ores, determination, 31
and alumina, catalytic power of, 119
Silicane, benzyl and benzyl ethyl derivatives of, 92
Silicon and palladium compounds, 299
organic derivatives of, 69, 92, 127
sulphides and oxysulphides, 272
Silver, electrolytic deposition, 137, 149
in complicated organic salts, determination, 192
in thallium, separation, 176
test for, 262
volumetric estimation of, 261
chloride and iodide, separation, 167
nitrate, action on inorganic hydroxides, 60
nitrite, molecular volume of, 176
selenide, compounds with selenides of arsenic, antimony, and bismuth, 288
Simonis, H., and M. Rindl. (*See* Rindl, M.)
Simonsen, J. L., ethyl 6-methyl-2-pyrone-3 : 5-dicarboxylate and its derivatives, 274
Sisley, P., and P. Barbier. (*See* Barbier, P.)
Slade, R. E., reducibility of magnesium oxide by carbon, 93
Slator, A., fermentation, 69
Smiles, S., dinitrodiphenylamine-o-sulphonic acids, 308
and E. de B. Barnett. (*See* Barnett, E. de B.)
and T. P. Hilditch, derivatives of *s*-phenylphenazothionium, 10
and R. le Rossignol, sulphination of phenolic ethers and influence of substituents, 154
Smirnoff, J., and O. Miller. (*See* Miller, O.)
Smith, Alice E., and K. J. P. Orton. (*See* Orton, K. J. P.)
C., and A. D. Mitchell, constitution of hydroxyazo-compounds, 166
S. W. J., and H. Moss, contact potential differences determined by means of null solutions, 129
W., murexide as a quondam dye-stuff and printing colour, 191
W., jun., simple and mixed esters of cellulose, 237
Snow, fertilising value, 243
Society of Chemical Industry, 45, 131, 190, 237, 286
of Dyers and Colourists, 144
Sodium, cutting, 73
benzylate, action of alcohols on, 143
nitrate and lead nitrate, mixtures of solutions of, 93
nitrite, manufacture, 237
sulphate solutions, spontaneous crystallisation, 166
sulphite, detection in presence of sodium sulphate and thiosulphate, 85
Solutions, apparatus for producing spark spectra of, 35
viscosity of, 261
Solvents, influence on rotation of optically active compounds, 262
Specialisation, danger of over, 106, 114
Spectra, absorption of crystals of, rare earths salts, 239
of hydrocarbons isolated from products of action of aluminium chloride on naphthalene, 308
of vapours of benzene and homologues, and of benzene solutions, 97
Spectra, spark, of solutions, apparatus for producing, 35
"Spectroscope" (review), 250
Spectrum top, 285
absorption, of camphor, 261
of triphenylmethane, 236
arc, spark lines in, 263
spark, of dysprosium, ultra-violet, 277
of yttrium, 250
Spencer, J. F., and Margaret Le Pla, quantitative separation of thallium from silver, 176
and Eleanor M. Stokes, direct interaction of aryl halides and magnesium, 8
Spielmann, P. E., origin of jet, 181
Stansbie, J. H., "Iron and Steel" (review), 250
Staudinger, H., and H. W. Klever, ketenes, 180, 192
"Steel, Iron and" (review), 250
"Steel and Iron Works Chemist, Practical Methods for" (review), 297
Steel corrosion, 31, 40
gases occluded in, 46
Stereoisomeric compounds, 262
Stevens, H. P., "Paper-mill Chemist" (review), 192
and C. Beadle. (*See* Beadle, C.)
Stewart, A. W., apparatus for determining specific inductive capacity of organic liquids, 262
Stewart, A. W., relation between dielectric constant and chemical constitution, 262
and N. T. M. Wilsmore. (*See* Wilsmore, N. T. M.)
Stock, A., phosphorus pentasulphide, 168
porous materials to replace cocks in working with gases, 60
vapour densities of P_4S_3, P_4S_7, P_2S_5, 203
E. Echeandia, and P. R. Voigt, decomposition of antimony hydride, 311
of arsenic hydride, 312
and F. Wrede, heat of formation of antimony hydride, 168
"Stoichiometry" (review), 178
Stokes, Eleanor M., and J. F. Spencer. (*See* Spencer, J. F.)
Stopcock and capillary connecting tube for gas burettes, 237
"Stow, George William, Life and Work of" (review), 297
Strecker, W., action of dimethylsulphate on alkaline polysulphides, 311
Strontium oxide, heat of formation of anhydrous, 142
Styrolene oxide, 250
Sublimation, apparatus for, 198
Substances containing a triple bond, action of ozone on, 59
influence of temperature on optical properties of dissolved, 47
time taken to dissolve, 298
which form a continuous series of mixed crystals, spontaneous crystallisation, 263
inorganic, triboluminescence of, 301
soluble, carrying down of by certain precipitates, 275
Sudborough, J. J., and J. M. Gittins, esterification constants of the normal fatty acids, 81
Sulphate, cuprous, ammoniacal, 119
Sulphobenzylethylpropylsilicyl oxides, optically active, 127
Sulphur, compounds of with iodides, 218
in organic matter, determining, 167
waste gases of Claus-Chance process, 85
anion and complex sulphur anions, 131
Sulphuryl chloride, action on selenium and selenium dioxide, 158
Swinton, A. A. C., and Hon. C. A. Parsons. (*See* Parsons, C. A.)
Syntheses by means of methyl and ethyl adipates, 95, 119
by mixed organo-metallic compounds of zinc. 179
Synthesis of ammonia, 119
brazilinic acid, the lactones of dihydrobrazilinic and dihydrohæmatoxylinic acids, anhydrobrazilic acid, &c., 129
calcium carbide and acetylene, 167
β-campholene lactone, 119
dihydromyrcene, 310
β—N—β / β—CHβ -dinaphthacridine, 8
β—CHβ isoxazoles, 311
1-methylcyclohexylidene-4-acetic acid, 307
pyranol salts related to brazilein and hæmatein, 308
racemic dihydro-camphoric acid, 117
terpenes, 135
Szilard, B., radio-lead, 119

TAFEL, J., and H. B. Thompson, electrolytic reduction of ethyl barbituric acids, 33
Talite, *d*-, crystalline, preparation and properties, 180
Tankard, A. R., and G. R. Thompson. (*See* Thompson, G. R.)
Tannins, constitution, 133
Tantalite in Australia, 203
Taylor, J., and A. E. Dixon. (*See* Dixon, A. E.)
Tellurium, atomic weight, 25, 209
gravimetric determination, 292
is it a mixture of two elements? 169
Temperatures of spontaneous crystallisation of mixed solutions, 93
Tempany, H. A., and F. Watts. (*See* Watts, F.)
Temperature equilibrium, dynamical analogues of, 156
Temperatures, influence of foreign substances on transition, 92
Terbium, 208
and dysprosium compounds, 75
Terpene, isolation of a new, 235
Terpenes, chemistry of, 93
synthesis of, 155
Tetrabromodiphenoquinone, 11
Tetramethyldiaminobenzhydrol, compounds with methylenic derivatives, 299
Tetramethyl glucose derivatives, 9
Tetranthera polyantha, var. citrate nees, esseonce of, 167
Tetrathionates, action of carbonates on, 144
Thallium and platinum alloys, 264
and silver, separation, 176
ion, existence of a subvalent in aqueous solution, 176
Thermo-chemical constants, calculation of, 183, 253, 266
"Thermochemistry" (review), 239
"Thermodynamics of Technical Gas-reactions" (review), 287
"Thermoelements and Thermopiles" (review), 298
Thetines, phenolic, and their action with benzoyl chloride, 262
Thiele, H., some reactions of ultra-violet light, 60
Thiocoumarins and coumarins, residual affinity of, 92
Thiocyanates containing an electro-negative group, constitution, 176
Thionyl chloride, action on methylene ethers of catechol derivatives, 128, 153
on selenium and selenium dioxide, 158
Thiophene derivatives, 240
Thiosulphocarbamates, metallic, properties of, 288
Thole, F. B. T., and A. E. Dunstan. (*See* Dunstan, A. E.)
Thomas, N. G., H. Hartley, and M. P. Applebey. (*See* Hartley, H.)
Thomas, V., derivatives of thiophene, 240
Thomlinson, J. C., experiments on waste gases of Claus-Chance sulphur process, 85
Thompson, G. R., and A. R. Tankard, determination of cocoanut oil in butter, 146
H. B., and J. Tafel. (*See* Tafel, J.)
Thomsen, J., "Thermochemistry" (review), 239
Thorianite, tin-group element in, 154
Thorium, 205
distribution in electric fields of active deposits of, 156
sulphur compounds of, 264
iodomercurate, 298
oxyfluoride and fluoride, 288
Thorpe, J. F., and C. W. Moore. (*See* Moore, C. W.)
T. E., atomic weight of radium, 229
centenary of Davy's discovery of the alkali metals, 193, 210
Threlfall, R., apparatus for experiments at high temperatures and pressures, and its application to study of carbon, 273
Thulium, 209
Tiffeneau, M., mechanism of formation of cyclic compounds in geranic series, 310

Tiffeneau, M., mechanism of phenyl transpositions in iodohydrins and aromatic glycols, 72
and Fourneau, MM. (*See* Fourneau, M.)
Tin, use as cathode for rapid quantitative electrolytic deposition of zinc, copper, silver, cadmium, and nickel, 137, 149
volumetric estimation, 13
group element in thorianite, 154
Titanium detection, 273
Titherley, A. W., labile isomerism among acyl-salicylamides and acyl-hydroxylamines, 177
Tizard, H. T., and N. V. Sidgwick. (*See* Sidgwick, N. V.)
Toluidides, *p*-, of normal fatty acids, melting-points of, 261
Tonge, J., "Coal" (review), 45
Top, spectrum, 285
Triazo-compounds, refraction and dispersion of, 259
Triazo-group, 129, 248, 306
Triboluminescence of inorganic substances, 301
Trichlorophenol, OH(1)Cl(2.4.6), and its transformation into chlorinated quinones, 250
Triphenylmethane, absorption spectrum of, 236
nature of impurity in preparations of, 236
orthobenzylated dyes from, 299
Tripheoylmethyl, preparation, 168
Trotman, S. R., "Leather Trades Chemistry" (review), 287
Tsakalotos, D. E., hydrates of fatty acids, 310
Turner, M. R., W. H. Perkin, jun., and R. Robinson. (*See* Perkin, W. H., jun.)
T., "Metallurgy of Iron" (review, 287
W. E. S., and A. N. Meldrum. (*See* Meldrum, A. N.)
Tutin, F., constitution of umbellulone, 91
and F. B. Power. (*See* Power, F. B.)

UMBELLULONE, constitution, 91
Unsaturation and optical activity, relation between, 154
Uranium, detection of helium in minerals containing, 275
Urbain, G., lutecium and neoytterbium, 157
ultra-violet spark spectrum of dysprosium and remarkable magnetic properties of this element, 277
and G. Jantsch, some compounds of terbium and dysprosium, 75

VACUUM distillation, manometer for, 128
tubes, helium, 95
use for drying hydrated salts, 48
Valency, 81
history of, 171
"Valentin's Practical Chemistry" (review), 95
Valeur, A., and C. Moureu. (*See* Moureu, C.)
Vanillin, new isomeride of occurring in root of a species of chlorocodon, 154
Vapour densities, determining, 27, 68, 102
of P_4S_3, P_4S_7, P_2S_5, 203
density apparatus, form of release for Victor Meyer's, 73
Vapours of benzene and homologues, absorption spectra, 97
"Varnishes, Analysis of Mixed Paints, Colour Pigments, and" (review), 287
Vegetable matter, analysis of, 152
Veley, V. H., affinity constants of bases as determined by the aid of methyl orange, 127
hydrolysis as illustrated by heats of neutralisation, 131
Verschoyle, W. D., periodic law, 225
Viguier, M., and M. Lespieau. (*See* Lespieau, M.)
Viscosity determinations at high temperatures, 308
of aqueous pyridine solutions, 153
of solutions, 261
Voigt, P. R., A. Stock, and E. Echeandia. (*See* Stock, A.)

WACKER, L., colorimetric method of determining the molecular weight of carbohydrates, 143
Wagner, H., and K. A. Hofmann. (*See* Hofmann, K. A.)
Wahl, A., and A. Meyer, derivatives of phenylisoxazolone, 240
Walden inversion, chemistry of, 235
A. F., and B. Lambert, "Systematic Introduction to Analytical Chemistry" (review), 287
Walker, A. J., and O. E. Mott, "Text-book of Organic Chemistry" (review), 71
W. H., Anna M. Cederholm, and L. N. Bent, corrosion of iron and steel, 31, 40
Walton, J. H., jun., and A. T. Lincoln. (*See* Lincoln, A. T.)
Water and pyridine mixtures, physico-chemical properties of, 91
and 2-methyl piperidine, mutual solubility, 261
determination of manganese in, 3
purification, 275
Water conductivity, preparation, 127
vapour, condensation in presence of radium emanation, 35
Waters, peaty, purification by freezing, 270
Plombieres, radio-activity of, 132
Watt, H. E., estimation of orcinol in orchella weed, 286
Wattmeters, dynamometer, 190
Watts, F., and H. A. Tempany, keeping power of Fehling's solution, 45
W. M., helium vacuum tubes, 95
Waves, alternate current, apparatus for demonstrating propagation of in cables, 189
Weber, W. H. Y., "Town Gas and its Uses" (review), 34
Weber, H. C. P., and W. A. Noyes. (*See* Noyes, W. A.)
Weidman, S., and V. Lenher, marignacite, 198
Weight, change in chemical transformation, 1
Weizmann, C., and W. H Bentley. (*See* Bentley, W. H.)
Wells' potassium lead periodide, composition and formula, 247
Werner's theory, criticism of, 262
Weston F. E., and H. R. Ellis, interaction of aluminium powder and carbon, 219, 233, 238
and C. W. Jeffreys, detection of sodium sulphite in presence of sodium sulphate and sodium thiosulphate, 85
R. S., determination of manganese in water, 3
Whitehead, C. S., examination of formulæ for grading of cables, 249
Widman, K. T., and J. Schmidt (*See* Schmidt, J.)
Wiesbaden Chemical Laboratory, 192
Wilks, W. A. R., and J. E. Purvis. (*See* Purvis, J. E.)
Will, W., glycerin nitrates, 311
Willgerodt, C., lecture experiments to prepare iodide chlorides, iodo and iodinium compounds, 251
Willstatter, R., and E. W. Mayer, reduction with platinum and hydrogen at ordinary temperature, 312
Wilsmore, N. T. M., and F Chick. (*See* Chick, F).
and A. W. Stewart, certain pyrogenic reactions, 11
Wolesensky, E., and V. Lenher. (*See* Lenher, V.)
Wolffenstein, R. and E. E. Peltner, barium percarbonate, 144
percarbonic acid salts, 144
Wologdine, S., and H. Le Chatelier. (*See* Le Chatelier, H.)
Woltereck, M., synthesis of ammonia, 119
Wood, J. K., amphoteric metallic hydroxides, 82
Woodhouse, J. C., and W. R. Lang. (*See* Lang, W. R.)
Woodiwiss, G., chemical elements, periodicity, weight, and valency, 122
some of the non-metallic elements in connection with valency and specific gravity, 265
Wool, influence of acids and bases on fixation of acid and basic dyes by, 47
Wrede, F., and A. Stock. (*See* Stock, A.)
Wren, H., and A. McKenzie. (*See* McKenzie, A.)
Wright, A. M., New Zealand boned beef, 50

O-XYLENE, nitro-derivatives of, 153

YATES, J., and R. H. Pickard. (*See* Pickard, R. H.)
Yeast-juice, fermentation of mannose and lævulose by, 259
Young, G., and A. E. Dunstan, chemistry of the amidines, 274
R. E., "The Life and Work of George William Stow" (review), 297
S. "Stoichiometry" (review), 178
W. J., and A. Harden. (*See* Harden, A.)
Ytterbium, 209
Yttrium, 208
phenomena in spark spectrum of attributable to positive electrons, 250
earths, 278
separation, 61

ZEH, W., and J. D'Ans. (*See* D'Ans, J.)
Zimmermann, F., and W. Biltz. (*See* Biltz, W.)
Zinc determination, volumetric method, 201, 215
electrolytic deposition, 89, 99, 137, 149
reductor, behaviour of molybdic acid in, 113
syntheses by mixed organometallic compounds of, 179
chloride, use in esterification of succinic acid, 112
cyanide, mercuric, 274
Zirconium, 205
a silicate of, 93
Zopf, W., "Die Flechtenstoffe" (review), 34

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NOTE ON THE QUANTITATIVE ESTIMATION OF LEAD IN ALLOYS.

By W. ELBORNE, M.A., and C. M. WARREN.

THE methods described in modern text-books on quantitative analysis for the estimation of lead in alloys, such as stereo and type metals, are exceedingly tedious and cumbersome; for instance, one of the methods advocated, operating upon 1 grm. of type metal, involves the use of aqua regia, 10 grms. of tartaric acid, 35 grms. of caustic soda dissolved in 500 cc. of water, boiling, saturating with sulphuretted hydrogen, filtering, boiling the precipitated sulphides in nitric acid till syrupy, diluting with water again, and filtering off traces of tin, evaporating with sulphuric acid, washing with alcohol, filtering, drying, igniting, and weighing as lead sulphate.

The process which we now introduce will be found to be very simple and to give quite as accurate results, and is applicable to all alloys of lead which are soluble in the solvent used. The principle of the process is based on the insolubility of lead chloride in absolute alcohol, whereas the chlorides of antimony, tin, arsenic, bismuth, iron, nickel, cobalt, manganese, copper, zinc, cadmium, aluminium, and magnesium are all soluble.

The process consists in taking 1 grm. of the alloy in fine shavings, placing it in a flask, and adding about 50 cc. of concentrated hydrochloric acid, then passing a slow current of chlorine gas through the liquid, in the cold, for some twenty-four hours; this is readily effected by adding some peroxide of manganese to concentrated hydrochloric acid in the cold in another flask, when, without application of heat, sufficient chlorine will be found to be continuously evolved, which is allowed to bubble through the liquid; after three or four agitations of the flask during the twenty-four hours, the whole of the alloy (stereo metal) will have passed into solution; in other more refractory alloys after saturation with chlorine the solution may be boiled, and the operation repeated until all is dissolved. When solution of the alloy is complete, transfer the liquid in small quantities at a time to a small weighed porcelain dish, and evaporate to dryness on a water-bath; allow to cool in a desiccator, then flood the dry residue with absolute alcohol, quickly stir with a glass rod, and immediately pour off the supernatant liquid through a dry weighed filter-paper; repeat this operation of washing with alcohol and filtration three or four times, allowing the last lot of alcohol to remain on the residue in the dish for five minutes before pouring off. Finally, transfer the dish with its contents, also the filter-paper, to a water-oven, and dry at 100° C. for three hours. Weigh as lead chloride, $PbCl_2$. The following is a specimen of the results obtained by the above process by merely pouring off the alcohol without any filtration, the slight deficiency in the amount of lead found being due to a small quantity of lead chloride poured off with the alcohol.

Known composition of alloy (grm.)	Lead	0·810	1·000
	Antimony .	0·150	
	Tin	0·040	
Lead chloride (grm.)			1·085
Equivalent to lead (grm.)			0·808

STUDIES OF THE PROCESSES OPERATIVE IN SOLUTIONS.*

By H. E. ARMSTRONG, F.R.S.

PART VI.—HYDROLYSIS, HYDROLATION AND HYDRONATION AS DETERMINANTS OF THE PROPERTIES OF AQUEOUS SOLUTIONS.

THE paper contains an account of a theory in explanation of the properties of solutions. Water is regarded as a complex mixture containing molecules of a variety of types; it is proposed to confine the term water to the mixture. It is argued that the active molecules in water are monad *hydrone* (H_2O) molecules and *hydrol-hydrone* (briefly *hydrol*) molecules, $H_2O{<}^{H}_{OH}$; the inactive, a series of polyhydrones of the form—

$$H_2O{:}OH_2, \qquad \begin{matrix} H_2O{-}{-}OH_2 \\ \diagdown\!\diagup \\ OH_2 \end{matrix}, \text{ \&c.}$$

When a substance RX is dissolved, if a non-electrolyte, in part it undergoes conversion into a hydrol $RX{<}^{H}_{OH}$; if capable of forming a conducting solution, it is not only hydrolated but itself in part *distributed* and converted into a hydrone of the type $H_2O{<}^{R}_{X}$: the mixture of these two isodynamic forms in solution constitutes a composite electrolyte, and electrolysis is the outcome of their reciprocal interaction under the influence of the current. The changes which take place in aqueous solution involve the interaction of such composite molecules—for example, when an acid is neutralised by an alkali—$HCl{<}^{H}_{OH} + NaHO{<}^{OH}_{H} = NaCl + 3H_2O$; the hydrol thus displaced forms water of the composition appropriate to the conditions prevailing in the solution. In this manner

* Abstract of a Paper read before the Royal Society, June 18th, 1908.

the large expansion is accounted for which attends the neutralisation of an acid by alkali. It is shown that the process is generally applicable.

Substances may also exist in solution in the form of *hydrones*, *e.g.*, NaCl : OH_2—in such compounds the water probably has greater optical effect than ordinary water : hence the increase of refractive power which in many cases attends dissolution in water.

THE REDUCTION OF VANADIC ACID BY ZINC AND MAGNESIUM.

By F. A. GOOCH and GRAHAM EDGAR.

A METHOD recently proposed by B. Glasmann (*Ber.*, xxxviii., 600) for the estimation of vanadic acid and molybdic acid in association with one another, depends upon the dissimilarity in the action of zinc and magnesium upon the former and the similarity in the action of these metals upon the latter in the presence of hydrochloric acid. The method consists essentially in treating for an hour to an hour and a-half, in a flask closed with a Bunsen valve, each of two aliquot portions of the solution containing a vanadate and a molybdate, the one with zinc and hydrochloric acid under gentle heating and the other with magnesium and hydrochloric acid, opening the flasks to the air, pouring the contents of each flask into a 500 cc. porcelain dish containing a solution of 10 grms. of manganese sulphate in 300 cc. of air-free boiling-hot water, and titrating with potassium permanganate while stirring actively. The amount of permanganate taken in titrating the contents of the first flask is used presumably in oxidising the molybdenum from the condition of Mo_2O_3 to that of MoO_3 and the vanadium from the condition of V_2O_2 to that of V_2O_5 : the amount of permanganate used in titrating the contents of the second flask shows presumably oxidation corresponding to a change of Mo_2O_3 to MoO_3 and to a change of V_2O_2 to V_2O_5. The difference between the amounts of permanganate used in the two titrations should presumably indicate the oxidation of V_2O_2 to V_2O_3 and so by calculation give the amount of V_2O_5 originally present in the solution. The amount of V_2O_5 having been determined, the amount of MoO_3 originally present is easily calculated from the amount of permanganate used in either titration.

It is plain that the value of the method depends largely upon the definiteness with which vanadic acid may be reduced to the condition of V_2O_3 by magnesium and left in the condition of V_2O_2 when the solution is treated with zinc and subsequently exposed to the air.

Concerning the reduction of vanadic acid by magnesium in the presence of hydrochloric acid, Glasmann gives the data and results of three experiments (Titrations Tabelle II., *loc. cit.*). Of these two are in fair agreement with the hypothesis ; but, unfortunately, the record of the third experiment is affected by an error of about 10 per cent, either typographical or of calculation. It is likewise interesting to note, though the conditions are different, that in Roscoe's study of the behaviour of vanadic acid in the presence of magnesium and sulphuric acid (*Ann. Chem. Suppl.*, 1868, vi., 77), to which Glasmann refers, the variation in the degree of reduction is likewise considerable, amounting to more than 2 per cent.

As to the reduction of vanadic acid by zinc, Roscoe's results show a degree of reduction approaching that of V_2O_2, but with variations of as much as 3 per cent ; and it is well known that the oxidation of solutions thus reduced proceeds rapidly and ultimately results in the condition represented by V_2O_4 (Roscoe, *loc. cit.* ; Gooch and Gilbert, *Am. Journ. Sci.*, xv., 390). Whether reductions may be kept regular and the action of air made so small as not to vitiate the analytical results of Glasmann's method during the short exposure, are matters for experimental determination. According to Glasmann's results in these experiments, the interference would seem to be inappreciable, but here again the calculated results are not in complete accord with the printed data (Titrations Tabelle I., *loc. cit.*).

It has seemed desirable, therefore, to consider further the accuracy which may be expected under the conditions of analysis in the reduction of vanadic acid by magnesium and by zinc.

Reduction by Magnesium.

Portions of a solution of sodium vanadate, standardised by the very accurate method of Holverscheit, were reduced by magnesium in the presence of hydrochloric acid or sulphuric acid (Inaugural Dissertation, Berlin, 1890).

In each of the experiments of Table I., A, the reduction was made, in a funnel-trapped flask, by magnesium in the presence of hydrochloric acid added gradually to properly moderate the action. After the magnesium had been used up, the contents of the flask were added to 800 cc. of boiled water containing 1 grm. of manganese sulphate and 2 cc. of sulphuric acid, and titration was made with nearly N/10 potassium permanganate. The conditions of the experiment were essentially those of Glasmann's method in respect to reagents and time of action.

In the experiments of Table I., B, the treatment was modified so that the action might be slower and long continued, with a view to bringing about better contact of the vanadium solution with the magnesium cushioned by evolved hydrogen. The reduction was made in a stoppered flask connected with a hydrogen generator, arranged for the maintenance of an atmosphere of hydrogen during the period of reduction, and fitted with a separatory funnel through which dilute sulphuric acid was added from time to time in small portions as required during the prolonged action, never evolving hydrogen violently enough to float the magnesium.

The experiments of Table I., C, were made to test the effect of using magnesium in the form of a heavy amalgam. About 2 grms. of magnesium were dissolved, with heating, in an excess of mercury, and the resulting liquid amalgam was used as the reducing agent, in the flask containing vanadic acid and sulphuric acid. At the end of the action, which took place without the application of heat and was over in about ten minutes, the distinctly violet solution was decanted, filtered from the mercury with careful washing, and titrated with potassium permanganate. Special tests in blank having shown that, for the amount of amalgam used, mercury goes into solution and acts upon the permanganate sufficiently to use up about 0·7 cc. of that reagent, a deduction of that amount from the total amount used was made for such action in each experiment, before calculating the degree to which the vanadic acid had been reduced.

From these results it is plain that the degree in which vanadic acid may be reduced by magnesium in the presence of hydrochloric acid or sulphuric acid is irregular and dependent upon conditions not easily controlled. With magnesium amalgam the reduction proceeds most readily and approximates more or less to the condition of V_2O_2.

It is obvious that under none of the conditions which we have tried is the reduction by magnesium sufficiently definite to be applied in a good analytical process.

In Table II. are given the results of the reduction of vanadic acid by zinc. The details of experiments made in the reduction flask with zinc and hydrochloric acid are given in A ; the record of experiments also made in the reduction flask with zinc and sulphuric acid is given in B ; and C contains the data of experiments made with the Jones reductor, in which a column of amalgamated zinc 40 cm. long and 2 cm. in diameter was used (Blair, "The Chemical Analysis of Iron," 6th Ed., 225). In all these experiments the titration was effected directly in air by nearly N/10 potassium permanganate. The V_2O_5 is calculated upon the hypothesis that the reduction goes to the condition of V_2O_2.

From the results of Table II. it is evident that in no case does the condition of oxidation of the product of the

TABLE I.

Time.	Magnesium met. Grms.	$KMnO_4$ N/10 × 1·052. Cc.	V_2O_5 taken as $NaVO_3$. Grm.	V_2O_5 calculated from oxidation of V_2O_3. Grm.	Error in terms of V_2O_5. Grm.	V_2O_2 reduced to— V_2O_3. Grm.	V_2O_2. Grm.
			A.—*Reduced by Magnesium and Hydrochloric Acid.*				
1 hour	4·0	26·05	0·1144	0·1249	+0·0105	0·0934	0·0210
1 ,,	4·0	26·2	0·1144	0·1257	+0·0113	0·0918	0·0226
1½ ,,	4·0	27·1	0·1144	0·1300	+0·0156	0·0834	0·0312
1½ ,,	4·0	28·3	0·1144	0·1357	+0·0213	0·0718	0·0426
			B.—*Reduced by Magnesium and Sulphuric Acid.*				
8 hours	4·0	24·1	0·1144	0·1156	+0·0012	0·1120	0·0024
8 ,,	4·0	23·8	0·1144	0·1142	−0·0002	—	—
8 ,,	4·0	25·2	0·1144	0·1208	+0·0064	0·1015	0·0129
8 ,,	4·0	25·4	0·1144	0·1218	+0·0074	0·0996	0·0148
16 ,,	8·0	26·5	0·1144	0·1271	+0·0127	0·0890	0·0254
16 ,,	8·0	26·1	0·1144	0·1252	+0·0108	0·0928	0·0216
20 ,,	12·0	26·8	0·1144	0·1285	+0·0141	0·0861	0·0283
			C.—*Reduced by Magnesium Amalgam and Sulphuric Acid.*				
				Calculated from V_2O_2.			
10 mins.	2·0	32·1	0·1144	0·1027	−0·0117	0·0353	0·0791
10 ,,	2·0	33·4	0·1144	0·1068	−0·0076	0·0228	0·0916
10 ,,	2·0	34·1	0·1144	0·1090	−0·0054	0·0161	0·0983
10 ,,	2·0	32·4	0·1144	0·1034	−0·0110	0·0329	0·0815
10 ,,	2·0	33·1	0·1144	0·1054	−0·0090	0·0269	0·0875
10 ,,	2·0	33·6	0·1144	0·1075	−0·0069	0·0208	0·0936

TABLE II.

Experiment.	$KMnO_4$. N/10 × 1·095. Cc.	V_2O_5 taken as $NaVO_3$. Grm.	V_2O_5 calculated from oxidation of V_2O_2. Grm.	Error in terms of V_2O_5. Grm.	Remarks.
		A.—*Reduced in Flask with Zinc and Hydrochloric Acid.*			
1.	35·0	0·1235	0·1166	−0·0069	Poured out into dish; titrated in presence of $MnSO_4$.
2.	35·85	0·1235	0·1194	−0·0041	
3.	34·9	0·1235	0·1163	−0·0072	
		B.—*Reduced in Flask with Zinc and Sulphuric Acid.*			
	N/10 × 1·0956.				
4.	36·3	0·1235	0·1203	−0·0032	Titrated in the reduction flask.
5.	36·4	0·1235	0·1209	−0·0026	
6.	36·2	0·1235	0·1213	−0·0022	
7.	36·05	0·1235	0·1206	−0·0029	
8.	36·1	0·1235	0·1201	−0·0034	
9.	35·68	0·1235	0·1188	−0·0047	Poured into dish for titration.
10.	34·8	0·1235	0·1159	−0·0076	Exposed in dish 20 minutes.
		C.—*Reduced by column of Amalgamated Zinc.*			
	N/10 × 1·052.				
1.	42·4	0·1381	0·1356	−0·0025	Titrated in the receiver exposed to the air.
2.	42·7	0·1381	0·1366	−0·0015	
3.	42·2	0·1381	0·1350	−0·0031	
4.	42·5	0·1381	0·1359	−0·0022	

TABLE III.

Ferric alum, 10 per cent sol. Cc.	Phosphoric acid, syrup. Cc.	$KMnO_4$. N/10 × 1·052. Cc.	V_2O_5 taken as $NaVO_3$. Grm.	V_2O_5 calculated from oxidation from V_2O_2. Grm.	Error in terms of V_2O_5 Grm.
25	5	43·10	0·1381	0·1378	−0·0003
25	5	43·20	0·1381	0·1381	—
25	5	43·30	0·1381	0·1384	+0·0003
25	5	43·28	0·1381	0·1384	+0·0003
25	5	43·32	0·1381	0·1385	+0·0004
15	3	21·60	0·0691	0·0690	−0·0001
15	3	21·62	0·0691	0·0691	—
15	3	21·80	0·0691	0·0696	+0·0005
40	8	64·90	0·2072	0·2075	+0·0003

reduction of vanadic acid by zinc and hydrochloric acid in the flask, by zinc and sulphuric acid in the flask, or by amalgamated zinc in the reductor, correspond exactly to V_2O_2 when titration is made in air. A series of experiments was made, therefore, in which care was taken to protect the reduced solution from the action of air until the highest degree of oxidation is past and registered, by an adaptation of a method used by Randall (*Am. Journ. Sci.*, xxiv., 313) for the accurate titration of molybdic acid similarly reduced by the column of amalgamated zinc. (We are indebted to Professor Henry Fay for the information that this mode of treating reduced molybdic oxide was first worked out many years ago by Dr. C. B. Dudley, though never published). According to this procedure, the receiver attached to the zinc column was charged with a solution of ferric alum, gentle suction was applied to the receiver, and in succession were passed through the column of amalgamated zinc, hot water (100 cc.), 2·5 per cent sulphuric acid (100 cc.), the solution of vanadic acid in 2·5 per cent sulphuric acid (125 cc.), and finally hot water (200 cc.). To the receiver was added syrupy phosphoric acid (4 cc.), to decolorise the solution, and the titration was made in the hot solution in the usual manner with potassium permanganate. Table III. contains the results of these experiments, corrected for the action of the zinc column upon the reagents without the vanadic acid.

The results of Table III. show plainly that the action of the column of amalgamated zinc carries the reduction easily and rapidly to the condition of V_2O_2, and that by anticipating the oxidising action of the air by means of a ferric salt in the receiver the solution is made less sensitive to the action of the air, while the highest degree of reduction is registered by the ferrous salt formed. A comparison of these results with those of Table II. shows unmistakably that a solution containing vanadium in the condition of V_2O_2 cannot be exposed to air, even momentarily, without undergoing oxidation.

Finally, it is evident that the assumptions upon which Glasmann's method for the determination of vanadic and molybdic acids is based—viz., that the condition of vanadium in a solution reduced by magnesium is definitely that of V_2O_3 and that the condition of vanadium in a solution reduced by zinc and exposed subsequently to the air is definitely that of V_2O_2—are unwarranted. — *American Journal of Science*, [4], xxv., p. 233.

THE ACTION OF VARIOUS ANHYDROUS CHLORIDES ON TELLURIUM AND ON TELLURIUM DIOXIDE.

By VICTOR LENHER.

In an earlier paper (*Journ. Am. Chem. Soc.*, xxiv., 188) the action of sulphur monochloride on elementary tellurium has been shown to result in the production of tellurium tetrachloride and sulphur, when the sulphur monochloride is in excess, while Krafft and Steiner (*Ber.*, xxxiv., 560), in studying this reaction, observed that when an excess of tellurium is heated with sulphur monochloride, tellurium dichloride results.

Further study on the action of tellurium and the dioxide with active reagents has shown that with many of the anhydrous chlorides, especially with those which are liquid at the ordinary temperature, tellurium tetrachloride is produced. In certain cases the tetrachloride immediately separates from the solution in pure form, while with a number of reagents of this character actual union takes place, and a crystalline condensation product separates.

Tellurium Dioxide and Sulphur Monochloride.—Tellurium dioxide, when treated with an excess of sulphur monochloride, is transformed into the tetrachloride, sulphur dioxide being formed at the same time, according to the equation $TeO_2+2S_2Cl_2=TeCl_4+SO_2+3S$.

Analysis, $TeCl_4$.—Calculated—Cl, 52·79; Te, 47·21. Found—Cl, 52·07; Te, 46·65.

When, on the other hand, an excess of tellurium dioxide is heated with sulphur monochloride, the reducing action of this reagent steps in, and the result is that the dichloride of tellurium is formed, thus:— $TeO_2+S_2Cl_2=TeCl_2+S+SO_2$.

The formation of tellurium tetrachloride by the action of excess of sulphur monochloride on tellurium dioxide takes place readily; the reaction can be materially hastened by warming, and under these conditions, preparation of a large amount of the tetrachloride can be accomplished in a very short time. Extraction of the salt with carbon bisulphide is advisable in order to remove an excess of sulphur.

Behaviour of the Oxychloride of Sulphur toward Tellurium and Tellurium Dioxide.—With thionyl chloride, either the oxide of tellurium or the metal yields tetrachloride when the anhydrous chloride is in excess, and dichloride when the element or oxide is in excess. These reactions are quite similar to the action of sulphur monochloride on the metal or oxide.

Sulphuryl chloride reacts with the element forming tellurium tetrachloride, but when the metal is in excess the dichloride is the resulting product. Tellurium dioxide in contact with sulphuryl chloride acts only very slowly, if at all, in the cold, but when the two are heated together in a sealed tube, crystalline products are formed which, by analysis, appear to be due to the simple solution of the dioxide in the sulphuryl chloride and subsequent recrystallisation of condensation products. The end products of the reaction are dependent on the reacting masses, and on the pressure at which the reaction is carried out.

Tellurium and Thionyl Chloride (with C. W. Hill).—Tellurium and thionyl chloride, when heated together in a sealed tube for twenty-four hours, yield crystals of the tetrachloride. The supernatant liquid was dark coloured, and was found to contain tellurium.

Analysis, $TeCl_4$.—Calculated—Cl, 52·79; Te, 47·21. Found—Cl, 52·00; Te, 47·47, 46·60.

In studying the action of thionyl chloride on tellurium it was found most satisfactory to heat the metal in a porcelain boat in a current of the vapour of thionyl chloride, which was produced by boiling thionyl chloride in a distilling bulb. The boat in which the tellurium was contained was placed in a combustion tube connected directly with the distillation bulb, and the combustion tube was drawn out into a series of bulbs. This apparatus was chosen inasmuch as the arrangement allowed the products of the reaction, by carefully regulating the temperature, to be carried from bulb to bulb, and in the first bulbs practically all of the sulphur formed in the reaction was retained, allowing the tellurium tetrachloride to be collected in the bulbs farthest from the boat.

Analysis, $TeCl_4$.—Calculated—Cl, 52·79; Te, 47·21. Found—Cl, 52·80, 52·20; Te, 47·01, 46·95.

The reaction of thionyl chloride on tellurium may be expressed, $2SOCl_2+Te=TeCl_4+SO_2+S$.

Thionyl Chloride and Tellurium Dioxide (with C. W. Hill).—By heating thionyl chloride with tellurium dioxide for twenty-four hours in a sealed tube, long slender crystals of tellurium tetrachloride were obtained. When the tubes in which the reaction was carried out were opened, sulphur dioxide was liberated.

Analysis, $TeCl_4$.—Calculated—Cl, 52·79; Te, 47·21. Found (I.)—Cl, 52·31, 52·71; Te, 47·11, 47·64. (II.)—Cl, 52·55, 52·13; Te, 47·55, 47·20.

On heating the dioxide in the vapour of thionyl chloride, tellurium tetrachloride is also readily obtained. Analysis II., above.

Sulphuryl Chloride and Tellurium (with C. W. Hill).—Tellurium and sulphuryl chloride, when heated together in a sealed tube, yield tellurium tetrachloride. On heating

tellurium in the vapour of sulphuryl chloride, the metal is first transformed into black dichloride, after which it is further chlorinated to the tetrachloride by the action of excess of the sulphuryl chloride.

Analysis, $TeCl_4$.—Calculated—Cl, 52·79 ; Te, 47·21. Found—Cl, 52·51, 52·36 ; Te, 47·14, 47·30.

Sulphuryl Chloride and Tellurium Dioxide (with C. W. Hill).—Tellurium dioxide acts quite differently toward sulphuryl chloride than it does with thionyl chloride or sulphur monochloride. When heated in the vapour of sulphuryl chloride to as high a temperature as it is possible to conduct an experiment in hard glass combustion tubing, there is apparently no action. No volatilisation of the tetrachloride occurs, and in our experiments, when a weighed amount of tellurium dioxide was heated in the vapour of sulphuryl chloride to as high a temperature as the glass would permit, the boat and contents weighed precisely the same after this treatment as before. This would indicate that under these conditions the vapour of sulphuryl chloride is without any appreciable action on tellurium dioxide.

When, however, tellurium dioxide and sulphuryl chloride are brought together in a sealed tube and heated, the system undergoes complex changes. When the dioxide was heated in a sealed tube with sulphuryl chloride for twenty-four hours at 165°, a small amount of a crystalline substance was formed, but the larger part of the dioxide remained unchanged. The heating was continued for seventy-two hours, when the dioxide completely disappeared, the liquid having assumed a dark yellow colour. On allowing the tube to cool, crystals deposited which were entirely unlike tellurium tetrachloride. When the tube was opened so much sulphur dioxide had been formed that the major part of the contents were lost when the pressure was released on opening the tube. The portion saved showed a content of 40·38 per cent of chlorine.

The experiment was repeated a number of times, the tubes being heated for forty-eight hours to 175°. In each case the tube was strongly cooled before opening, and in each tube a crystalline product was obtained.

Analysis showed the crystalline substances formed to vary in composition. Their composition by the analytical data obtained may be indicated as follows :—$3TeO_2.4SO_2Cl_2$; $5TeO_2,9SO_2Cl_2$; $TeO_2,2SO_2Cl_2$; $2TeO_2,5SO_2Cl_2$.

Sulphuryl chloride appears to have no action on tellurium dioxide at the ordinary temperatures, or when the dioxide is heated in the vapour of sulphuryl chloride, but when the two are heated together to high temperatures in a sealed tube, condensation products of varying composition are obtained.

In each experiment it was found that the excess of sulphuryl chloride contained large quantities of tellurium.

General Remarks.

In studying the action of the chloride of sulphur or the oxychlorides of sulphur it is observed that not infrequently one of the products of the reaction along with tellurium chloride is sulphur dioxide. Frequently in our experiments, in sealed tubes, large volumes of sulphur dioxide escaped on opening the tubes, while in the tube itself pure white tellurium chloride remain. This is an interesting illustration of mass action, as well as of conditions in the system, since sulphur dioxide readily precipitates tellurium from an aqueous or acid solution of the chloride, and the dioxide when heated in a current of sulphur dioxide gas is readily reduced to metal.

While the action of the various chlorides of sulphur on tellurium or on tellurium dioxide goes on readily, a number of other anhydrous chlorides act similarly, but not infrequently by-products are formed which contaminate the chloride of tellurium which is produced. For example, *arsenic trichloride* or *antimony trichloride* react with tellurium dioxide, yielding tellurium tetrachloride and arsenic trioxide, or antimony trioxide. In these cases it is very difficult to obtain the tellurium chloride in a high degree of purity. *Lead tetrachloride* will convert either the element or the oxide to tellurium tetrachloride. Here, again, an impure salt is formed, and a mixture is obtained from which it is difficult to obtain pure tellurium salt.

Phosphorus trichloride, in contact with the dioxide of tellurium, quickly reduces it to the elementary condition, and when brought in contact with the element in pure condition is without action.

Carbon tetrachloride is without action on tellurium or on tellurium dioxide even when allowed to be in contact with either of them for a great length of time.

Tellurium Dioxide and Antimony Pentachloride.—Antimony pentachloride reacts with tellurium dioxide in the cold, the action of heat materially hastening the reaction, with the formation of the compound $TeCl_4SbCl_5$.

Analysis, $TeCl_4.SbCl_5$.—Calculated—Te, 22·49 ; Sb, 21·16 ; Cl, 56·35. Found—Te, 22·02 ; Sb, 21·74 ; Cl, nil.

The action of antimony pentachloride on tellurium dioxide can be considered as first resulting in tellurium tetrachloride, which immediately unites with an additional molecule of antimony pentachloride, forming the addition product $TeCl_4SbCl_5$:—

$$(a)\quad 5TeO_2 + 4SbCl_5 = 5TeCl_4 + 2Sb_2O_5\ ;$$

$$(b)\quad TeCl_4 + SbCl_5 = TeCl_4,SbCl_5\ ;$$

or—

$$5TeO_2 + 9SbCl_5 = 5[TeCl_4,SbCl_5] + 2Sb_2O_5.$$

The compound $TeCl_4.SbCl_5$ appears in white tabular crystals which are readily decomposed by water.

Phosphorus Oxychloride and Tellurium Dioxide.—When phosphorus oxychloride is brought in contact with tellurium dioxide and the two are allowed to remain together in a warm place, a crystalline mass of large flat monoclinic plates begins to form. The excess of phosphorus oxychloride can be readily removed by means of carbon bisulphide. These crystals are deliquescent, and are readily decomposed by water.

Analysis, $TeCl_4.POCl_3$.—Calculated—Te, 31·32 ; P, 7·61 ; Cl, 61·06. Found—Te, 30·22 ; P, 7·90 ; Cl, 59·13.

While phosphorus oxychloride doubtless first reacts with tellurium dioxide to form tellurium tetrachloride, the tetrachloride, as soon as produced, unites with one molecule of the excess of phosphorus oxychloride forming the addition product. The first reaction could be indicated $3TeO_2 + 4POCl_3 = 3TeCl_4 + 2P_2O_5$, and the entire reaction may be expressed $3TeO_2 + 7POCl_3 = 3[TeCl_4.POCl_3] + 2P_2O_5$.

When the above reaction is carried out with an excess of phosphorus oxychloride, a considerable portion of the reaction product remains in solution in the excess of the reagent.

It thus appears that by the action of the various anhydrous chlorides which have been studied on tellurium or tellurium dioxide, three series of products can form ; either tellurium tetrachloride or the dichloride can be produced, or by the use of such compounds as phosphorus oxychloride or antimony pentachloride, double chlorides can be obtained.—*Journal of the American Chemical Society*, xxx., No. 5.

Neutral Triple Sulphates of Calcium.—J. D'Ans.—Solutions of copper sulphate give with potassium syngenite in salt solutions a new crystalline substance which is analogous to polyhalite $Ca_2MgK_2(SO_4)_2.2H_2O$, but contains copper instead of magnesium. The investigation of corresponding triple sulphates of calcium shows that the magnesium in the salts of formula $Me.SO_4.Me_2SO_4.6H_2O$ or $4H_2O$ can be replaced by copper, cadmium, nickel, cobalt, iron, manganese, or zinc, while the potassium can be replaced by ammonium, rubidium, or cæsium. Sodium does not give a triple sulphate with calcium. These new polyhalites crystallise very eadily.—*Berichte*, xli., No. 8.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

PART III.—ANALYSIS OF THE ALUMINIUM AND IRON GROUPS, INCLUDING BERYLLIUM, URANIUM, VANADIUM, TITANIUM, ZIRCONIUM, AND THALLIUM.

By ARTHUR A. NOYES, WILLIAM C. BRAY, and ELLWOOD B. SPEAR.

Introduction.

THIS article is a continuation of a preceding one (*Journ. Am. Chem. Soc.*, 1907, vol. xxix., p. 137 *et seq.*), in which were presented the first two parts of this system of qualitative analysis, dealing respectively with the preparation of the solution, and the analysis of the silver, copper, and tin groups (see CHEMICAL NEWS, vol. xciii., p. 134 *et seq.*; xcv., p. 89 *et seq.*). For the purposes of this investigation, for the general considerations underlying it, and for various conventional matters relating to its presentation, the reader is referred to the introduction to the preceding paper.

Although the final form of the scheme of analysis of the groups here considered has been worked out during the past year by the authors of this article, much of the preliminary experimental work, especially that relating to the rarer metals, was carried on by others in the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology. It is, unfortunately, scarcely practicable to indicate in just what respects each of these investigators has contributed to the final result; but we wish to express in a general way our great indebtedness to Messrs. Howard I. Wood, Bart E. Schlesinger, and Charles Field (3rd) for the assistance which their work has been to us.

The present publication deals with the analysis of the precipitate produced by ammonium hydroxide and sulphide in the filtrate from the hydrogen sulphide precipitate. In addition to the seven common elements (nickel, cobalt, iron, manganese, zinc, chromium, and aluminium) considered in almost all schemes of qualitative analysis, we have included six of the especially important rarer elements, namely, beryllium, uranium, vanadium, thallium, titanium, and zirconium. The portions of the procedure and of the notes referring to these rarer elements are, however, marked with asterisks, so that they may be readily omitted by any one interested only in the common elements.

The general features of our scheme for the analysis of this solution will be most readily comprehended by an examination of the tabular outline presented in Tables VII. to IX. The considerations which have led to the adoption of this procedure will be discussed in the next chapter entitled "General Discussion," and the detailed process and the explanations of it will be presented in the following one entitled "Procedure and Notes." Later chapters, as in the preceding publication, will be devoted to the "Test Analyses and to Confirmatory Experiments and References."

General Discussion.

1. With respect to the original precipitation of these elements, schemes of qualitative analysis differ as to whether ammonium hydroxide and ammonium sulphide be used successively with a filtration between, or whether they be added together so that all the elements are contained in a single precipitate. The former of these methods has the serious disadvantage that the separation with ammonium hydroxide of the trivalent elements, aluminium, chromium, and ferric iron, from the bivalent elements, nickel, cobalt, manganese, and zinc, while satisfactory enough when certain combinations of these elements are present, is not so for other combinations. Thus even a large quantity of zinc may be quantitatively precipitated by ammonium hydroxide when a larger proportion of chromium is present; and manganese will in any case be partially precipitated by that reagent owing to its oxidation by the air to the manganic state, and it will be completely precipitated when phosphate is present in the solution. It is therefore necessary to provide for the detection of zinc and manganese both in the hydroxide and in the sulphide precipitate; and thus the scheme is complicated rather than simplified by precipitating separately with these reagents.

We have therefore adopted the plan of a single precipitation by simultaneous addition of both reagents, provision being made, however, for observing the effect of the addition of ammonium hydroxide alone for the sake of the indications which it may furnish. If care be taken to avoid an unnecessary excess of both the hydroxide and sulphide, all the elements in question are completely precipitated by these reagents even in moderately dilute solution with the exception of a little of the nickel and a variable proportion of the vanadium. The nickel can be removed from the filtrate by boiling. Even a large quantity of vanadium remains completely in solution when it is present alone; but, on the other hand, it may be almost completely precipitated, probably as a hypovanadate or vanadate, when certain other elements of these groups are present. Many experiments were made in this laboratory by Mr. Charles Field (3rd) to devise a practical method of reducing vanadium to a vanadous salt (corresponding to the oxide, V_2O_3) in which state it is completely precipitated by ammonium hydroxide. In accordance with the results of Gooch and Curtis (*Am. Journ. Sci.*, 1904, [4], xvii., 45) hydriodic acid (best in the form of a mixture of ammonium iodide and hydrochloric acid) was found to be the only available agent, but even with the aid of this reagent reduction and precipitation were never quite complete, and sometimes did not take place at all. For this reason it was not considered worth while to use this reagent, especially since the vanadium can be removed from the ammonium sulphide filtrate by acidifying, adding ferric chloride, and making alkaline with ammonia.

2. The ammonium sulphide precipitate in all the schemes of analysis known to us is first treated with cold dilute hydrochloric acid, in order to separate nickel and cobalt from the other elements. In spite of the general use of this process, we have become convinced that it does not fulfil the requirements of exact qualitative analysis; for not only is it true, as is generally known, that a considerable quantity of nickel and cobalt dissolves in a mixture of 1 volume of HCl (1·12) with 5 volumes of water when there is a large residue containing these elements, but our experiments have shown that a moderate quantity of either of them (up to at least 5 mgrms.) may *completely* dissolve, and thus escape detection when it was originally disseminated through a large precipitate of iron sulphide. We have therefore eliminated this treatment as a method of separation, and, after adding hydrochloric acid at first to decompose such of the sulphides as will act upon, and to get an indication as to the presence of much nickel or cobalt, nitric acid is added, so as to bring all the elements into a single solution. Incidentally it may be mentioned that our experiments support the view that the fact that nickel and cobalt sulphides, though not precipitated by hydrogen sulphide from a slightly acid solution, yet dissolve difficultly in a much stronger acid, is due to an abnormally slow rate of solution of these sulphides, which are, in fact, relatively soluble substances, at least in the freshly precipitated state. For these experiments have shown that nearly all of a portion of the precipitated nickel sulphide dissolves when treated with successive portions of cold dilute HCl (1 volume HCl, 1·12, with 5 volumes of water) even when the acid is kept saturated with hydrogen sulphide, and that solution continues to take place even after considerable nickel (30 mgrms. in 30 cc.) has passed into solution. When, therefore, the surface exposed to the acid is greatly increased, either by the residue being a large one or by a small residue being left in a finely divided state by the dissolving out of iron sulphide, a considerable quantity of nickel and cobalt passes into solution in a comparatively short time. It is interesting to note that the

* From the *Journal of the American Chemical Society*, xxx., No. 4.

reverse reaction, the precipitation of nickel sulphide by hydrogen sulphide in acid solution, also takes place very slowly, for Baubigny (*Comptes Rendus*, 1882, xciv., 963 *et seq.*; xcv., 35) has observed that in the presence of acetic acid, or of very small amounts of sulphuric or hydrochloric acids, the precipitation is a slow but continuous process.

3. Having now all the elements together in solution, the next step in our process is to divide them into two main groups by the addition of sodium hydroxide and peroxide, followed by subsequent boiling. This method has been previously applied by other authors to the separation of certain of the common elements, but not, we believe, as a general means of subdivision. These reagents cause the complete precipitation of iron, nickel, cobalt, and thallium, as hydroxides of the trivalent form, and of manganese, titanium, and zirconium as hydroxides of the quadrivalent form. We shall designate all these elements so precipitated as the "iron group." All the remaining elements, namely, aluminium, beryllium, zinc, chromium, uranium, and vanadium, remain in solution in the form of sodium salts of the corresponding acids, namely, as aluminate, zincate, chromate, peruranate, and vanadate. We shall designate all these elements so dissolved as the "aluminium group." The separation of the two groups by this process is entirely satisfactory, at any rate, from the standpoint of qualitative analysis, with the single exception that when only 5 or 10 mgrms. of zinc are present, this may be carried down completely when elements of the iron group (especially manganese) are present in large quantity. This makes it necessary to provide for the detection of zinc in the analysis of the precipitate when it is large, but this is not attended with special difficulty. The use of sodium peroxide has the distinct advantage over that of sodium hydroxide alone, that chromium, uranium, and vanadium are taken completely into solution, whereby not only a division of these elements between the precipitate and filtrate is avoided, but also the carrying down of zinc into the precipitate is made less common and less considerable.

4. Since, owing to the possible presence of phosphate, oxalate, or hypovanadate in the original solution, the alkaline-earth elements may be precipitated by ammonium hydroxide and sulphide, sodium carbonate is added with the hydroxide and peroxide, in order to ensure the complete precipitation of these elements (more especially barium) with the iron group. The presence of phosphate and carbonate does not affect at all the separation of the elements of the aluminium and iron groups from each other.

5. The separation of the elements of the aluminium group from each other is very simple when only the common elements, chromium, aluminium, and zinc, are to be provided for, and the process recommended below for this case offers no original features. It consists in precipitating the aluminium hydroxide from the solution with ammonium hydroxide after acidifying with nitric acid, the chromate in the filtrate with barium chloride after acidifying with acetic acid, and the zinc with hydrogen sulphide in the filtrate from the barium chromate.

(To be continued).

Isomeric Aminophenylarsenic Acid.—A. Bertheim.—When arsenic acid is heated with aniline *p*-aminophenylarsenic acid, $NH_2.C_6H_4.AsO(OH)_2$, is obtained. When phenylarsenic acid is nitrated a nitrophenylarsenic acid is formed which Ehrlich and Bertheim suggested should yield the isomeric meta-amino-acid on reduction. But reducing agents readily attack the arsenic acid residue. If, however, sulphuretted hydrogen is used and the sulphur is removed by a copper salt, the meta-aminophenylarsenic acid is obtained; or sodium amalgam, which does not affect the arsenic acid residue, can be used for the reduction. It is not quite certain whether the new acid (which differs in physical and chemical properties from the para acid) is the ortho or meta derivative, but it is most probably the latter.—*Berichte*, xli., No. 8.

UNIVERSITY OF CAMBRIDGE.

Honours for Men of Science.

On June 17th Honorary Degrees were conferred on the following men of eminence in Science, Literature, and the Arts:—The Right Hon. H. H. Asquith, The Duke of Northumberland, The Earl of Halsbury, Admiral Sir John Fisher, Sir Hubert von Herkomer, The Hon. C. A. Parsons, The Right Hon. Sir G. O. Trevelyan, Bart., Sir James H. Ramsay, Bart., Sir Andrew Noble, Bart., Sir William Crookes, Mr. Rudyard Kipling, Professor Horace Lamb, Professor G. D. Liveing, Mr. Alfred Marshall.

Dr. Sandys, the Public Orator, spoke as follows in presenting to the Chancellor the two chemists who were among the recipients of the Honorary Degree of *Doctor Scientiæ*. "Dignissime domine, domine Cancellarie, et tota Academia:—

"Cancellarii nostri auspiciis nunc demum eum ipsum praesentem videmus quem diu desideravimus, quem alia ex alia scientiarum in studiis occupata Societas praesidem suum olim suspexit. De scientia chemica et physica exploranda per annos plus quam quinquaginta praeclare meritus, in rerum primordiis primis spectri (ut aiunt) auxilio examinandis eam ipsam provinciam feliciter exploravit, quae etiam scientiae physicae in officina nostra maximo cum fructu indagata est. In observando quam acutus est, in experiendo quam peritus, in rebus difficillimis investigandis quam pertinax! Viri tanti exemplo Vergili dictum denuo praeclare confirmatum est:—'Labor omnia vicit improbus.'

"Duco ad vos Regiae Societatis socium, virum numismate Copleyano honoris causa haud ita pridem donatum, equitem insignem, Willelmum Crookes."

"Abhinc annos duo et sexaginta Cantabrigiam primum petivit vir intra proximum quinquennium in disciplina mathematica et in rerum naturae studiis honores summos adeptus, qui, post itinera sua Berolinensia, scientiae chemicae inter nosmet ipsos docendae sese strenue dedicavit, et Divi Ioannis in Collegio primam scientiae illius officinam Cantabrigiensem aedificandam curavit. Postea Universitatis professor nominatus, horum studiorum officinae amplissimae publice condendae summan diligentiam, summam operum exterorum experientiam, feliciter adhibuit. Lucis vero radiis spectri (ut aiunt) ope retexendis, et rerum naturae penetralibus examinandis, quot annorum labores dedicavit! quot discipulis studiorum uno tenore assidue peractorum exemplar quam pulchrum praebuit! In operibus bonis adiuvandis liberalissimus, in negotiis academicis partium liberalium defensor indefessus, per tot annos inter tantas rerum vicissitudines animum serenum, aequum, prudentum, modestum conservavit. Virum talem preconio eodem dignum esse crediderim, quo populi Americani praeses quidam magnus, professoris nostri in anno primo munus suum ingressus, populi sui a poeta eximio postea est laudatus:—

> En vir benigne intentus, fortis, providus,
> Sagax patiensque, laudem non culpam timens.

"In laboribus suis ad exitum felicem perducendis per annos plurimos supersit Collegii sui socius perpetuus, scientiae chemicae professor emeritus, Georgius Downing Liveing."

(*Translation*).

Sir William Crookes.

Under the auspices of our Chancellor we now have before us one we have long desired to see, a man whom so many scientific Societies have claimed as their President. For more than fifty years he has greatly distinguished himself in chemical and physical research. The investigation of the spectra of the so-called primordial elements he has made his own special province—a province also which has been explored not unsuccessfully in our own laboratories of physical science. As an observer how acute he is! As an experimentalist how skilful! In overcoming diffi-

culties how persistent! In such as he we see once more signally confirmed the well-known statement of Virgil:—"Labor omnia vicit improbus." (All difficulties yield to strenuous toil).

I present to you a Fellow of the Royal Society, a recent Copley Medallist *honoris causa*, the worthy Knight, WILLIAM CROOKES.

PROFESSOR G. D. LIVEING.

Sixty-two years ago he first entered Cambridge; in the next five years he obtained the highest honours in Mathematics and Physical Science. After a residence in Berlin he earnestly devoted himself among us to the teaching of chemistry; at St. John's he superintended the building of the first laboratory for that science. Subsequently appointed Tutor in the University, he applied with success his great experience in other fields of labour, his great diligence in building a very complete public laboratory for this science. In revealing the secrets of the spectrum and in investigating the problems of Nature, what years of toil did he spend! and to how many of his scholars did he afford at the same time an excellent example of much work assiduously performed. Most liberal in assisting good work, in the business of the University he was an untiring champion. During all this time, in all these vicissitudes he preserved a calm demeanour, an evenly balanced mind, and exhibited the greatest modesty. He is worthy of the same compliment as a certain President of the United States who entered upon his office in our Professor's first year: he received the following laudatory notice from the poet Lowell:—

"Behold a man, kind, energetic, brave,
Farsighted, patient, fearing praise more than blame."

In his labours, carried out to his resignation, for many years he has been a life-member of our College, a worthy Professor of Chemistry, GEORGE DOWNING LIVEING.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Special General Meeting, June 12th, 1908.

Dr. CHARLES CHREE, F.R.S., President, in the Chair.

A SPECIAL General Meeting was held at which the resolution passed at the Special General meeting on May 22nd was confirmed.

An Ordinary Meeting of the Society was then held.

A paper by Messrs. E. BELLINI and A. TOSI on "*Experiments on a Directive System of Wireless Telegraphy*" was read by Mr. Tosi.

The authors describe the results obtained in the course of their work upon a further development of their original directive system.

In the earlier method previously described (*Electrical Engineering*, 1907, ii., 771; 1908, iii., 348) it was not possible to say from which side of the receiving station the transmitted waves arrived, for though the radiation was practically confined to the plane of the aërial system, it was emitted equally in the opposite direction to that desired.

In the new unilateral system the waves are sent in a single direction only, and the problem of getting rid of the backwardly extending radiation has thus been solved. The method adopted consists in superposing a bilateral directive system, as previously described, upon an ordinary or vertical antenna system. Since the two half diagrams of the directive aërial are opposed in phase, it follows that when the two systems (directive and vertical antenna) are simultaneously excited and in phase, the one half of the directed radiation will add itself to, and the other subtract itself from, the radiation due to the vertical antenna system. The diagram of the vertical antenna system being a circle, the resultant diagram of the superposed systems will, for the case where these are in phase as regards excitation, be a cardioid whose maximum radius vector is double that of the diagram of the directive system alone. Since then the directive system is able to vary the direction of its maximum emission by means of the radiogoniometer, it follows that by moving the position of this latter it is possible to shift the direction of the resultant emission represented by the cardioid, in a corresponding manner. Several energy diagrams obtained by means of the thermo-galvanometer are reproduced in the paper, and these show that, even where the excitations are not exactly in phase, the only result is a slightly less good diagram. Diagrams of the scheme of connections employed during the taking of the energy diagrams are also given.

The same principle of the superposition of the two systems has been applied to the case of the reception. In this case a phase displacement of 90° in the excitations is produced in a suitable manner, and in this way, when the pointer of the radiogoniometer is directed, say, towards the transmitting station, the reception is a maximum, whilst when turned at 180° from this it is a minimum, or zero. Diagrams of received energy and of the connections employed are also given in this case.

The system of unilateral directive wireless telegraphy described in the present paper is of special interest owing to the facility with which it is possible to change over from one system to the other; thus, from the ordinary vertical antenna system to the bilateral directive or the unilateral directive, or *vice versâ*. The aërial arrangements, moreover, remain exceedingly simple.

When a message from a station of unknown position is expected, the vertical antenna or ordinary system would be employed; on once effecting reception, one can pass to the bilateral or unilateral directive system, and thus determine the direction and on which side the transmitting station lies, at the same time making oneself independent of other transmissions.

In the same way, with the transmission, the vertical antenna would be employed for calling up an unknown station, or for simultaneously sending to several stations; on once getting a reply the operator can then readily determine the position of the receiving station, with the aid of the unilateral system, and thenceforth will transmit solely in that direction.

Attention is called to the advantages which such a directive system offers in the case of the commercial services as well as for military and naval purposes.

Dr. FLEMING said that he had long been acquainted with the interesting experiments of the authors of this paper, and desired to express his congratulations on the skill and inventiveness with which these investigations had been prosecuted. He was glad to see that the experiments of the authors confirmed in many ways the theory which he (Dr. Fleming) had given of the operation of a bent antenna as employed by Mr. Marconi.

When Mr. Marconi read his paper at the Royal Society in March, 1906, describing his experiments on directive telegraphy he gave no theory in the matter, but Dr. Larmor pointed out in the discussion that an antenna partly vertical and partly horizontal was equivalent to the sum of a magnetic oscillator and an electric oscillator, and shortly afterwards he (Dr. Fleming) had gone more carefully into the matter mathematically, and showed that the observed effects could be accounted for on this theory.

Both Mr. Marconi and he himself had obtained by the same methods as those employed by Messrs. Bellini and Tosi the same type of pear-shaped radiation curves obtained by the authors of the paper by combining together the effect of closed and open oscillators. Although this theory had been criticised by Dr. Mandelstam lately, yet nevertheless there did not seem sufficient grounds for objecting to it. Mr. Marconi had, as everyone knew, employed directive antennæ for a long time past in his power stations at

Poldhu and Clifden, and had also given demonstrations showing that the position of ships out of sight could be located by means of such receiving directive antennæ. Nevertheless, Messrs. Bellini and Tosi had worked out extremely ingenious arrangements for determining the direction of the radiant point without moving the antennæ themselves. He (Dr. Fleming) had also shown that, having the power to locate the radiant point, two stations equipped with such antennæ at a known distance apart could by simultaneous observations determine also the distance of the radiant point, and this might become important in connection with marine work.

It ought also to be noticed that Dr. F. Braun, of Strasburg, had by the employment of three open antennæ having oscillations in them of definite phase difference, been able to obtain radiation curves having the form of a cardioid similar to some of those given by the authors of the paper.

Dr. W. H. Eccles warmly congratulated the authors upon their beautiful and original method. On this method, by merely rotating a small coil of wire on the table, a fixed aërial directive system of any size was made to do what could otherwise only be done by turning the whole system of aërial wires in azimuth. The essence of the system was the piece of apparatus styled the radiogoniometer, which, by causing appropriate component radiation from two fixed wire triangles set at right angles, brought about a resultant radiation in any direction desired—just as if a virtual aërial of the full size of the fixed aërials were being rotated in the air. Someone had compared the result so achieved with that obtained by Marconi's well-known arrangement of a number of fixed bent antennæ with their horizontal portions directed from a centre to various points of the compass. Apart from the fact that it is rarely feasible to fix up a large number of antennæ, the radiogoniometer method has the advantage that the direction of transmission or reception can be altered perfectly smoothly ; so that if it can be used, as stated by the authors, accurately to about 1° of arc, the radiogoniometer is the practical equivalent of 360 bent antennæ.

The looped aërials used by the authors did not seem to the speaker to be the best kind of radiator for utilising the principle they had developed. The radiogoniometer would prove to be capable of giving excellent results with two fixed antennæ of the bent type set at right angles, one, for example, in the meridian plane and the other in the east-west plane. The two looped aërials of the authors may each of them be assimilated to a pair of vertical antennæ emitting waves of 180° phase difference, and with the assumption that for a single vertical aërial the inverse square law holds for the propagation of electrical effects from a single aërial, the speaker showed by aid of the ordinary equation of wave-motion that a looped antenna obeying the condition stated emitted two waves of equal period, of phases differing 90° and 180° respectively from the phase of the radiation from either side of the loop, and of amplitudes having a ratio proportional to λ/x. This means that one portion of the resultant radiation obeys an inverse square law and the other portion an inverse cube law; the latter portion is the more important of the two when the distance x is small, the former is the more important when the distance x is much greater than the wave-length λ. This explains why Dr. Fleming's measurements of the radiation from closed oscillators, which were carried out at short distances, gave small promise of powerful propagation to a distance, and why Messrs. Bellini and Tosi had found as a fact that good propagation occurred to great distances.

As regards the phases of the two portions of the radiation, the important portion for wireless telegraphy, namely, that obeying the inverse square law, was 90° out of phase with the near side of the loop ; and thus it is clear that the vertical aërial the authors had used to cancel the radiation to one side of the sending station, must for that purpose emit radiation 90° out of phase with the near side of the loop. Messrs. Bellini and Tosi had reached this conclusion in the course of their experiments.

After eliciting that the power-supply to the primary of the induction-coil for the Dieppe-Havre experiments was 500 watts, Dr. Eccles concluded by remarking that the authors were worthy of special congratulation because in their method of unilateral transmission by phase and intensity adjustment of several radiators they had eluded the difficulties of managing the phases that had apparently baffled F. Braun when he was using the same principle.

Mr. W. Duddell complimented the authors upon their paper, and asked for the wave-length of the waves given out by the transmitter. He also asked what would be the effect of opening the closed antennæ at the top.

Mr. Tosi, in reply to Dr. Fleming, stated that Braun's cardioid diagram was a theoretical diagram only ; the method had not succeeded, and no actual diagram obtained experimentally had ever been shown.

Referring to the similarity which Dr. Fleming said the pear-shaped diagram of Marconi bore to the authors' diagrams, Mr. Tosi could only say that they had purposely shown some bad diagrams as well as some good ones. The good diagram of Marconi's corresponded to the authors' bad diagram. With the Marconi horizontal aërial it would, moreover, be necessary, as Dr. Eccles had pointed out, to employ 360 such wires to obtain an accuracy in locating the bearing of the radiant point equal to that secured with the system now described. Further, if the emitted energy is actually represented by Marconi's pear-shaped diagram, it is difficult to understand why the transatlantic messages from Clifden to Glace Bay are readily picked up off the Algerian coast, at right angles to the line of transmission.

In reply to Mr. Duddell he said that the wave-length of the waves employed was from 350 to 400 metres.

A paper "*On the Lateral Vibration and Deflection of Clamped-directed Bars*" was read by Dr. J. Morrow.

This is an investigation of the problems which arise in connection with the lateral vibrations of clamped-directed bars. The term "directed" is used to describe the extremity of a bar which is constrained to maintain its original direction, but is free to take up any position of lateral deflection. These terminal conditions are mentioned in Rayleigh's "Sound," but are dismissed on the ground that the directed end cannot be realised experimentally. In the present paper, however, it is shown that the "directed" end is of great importance and of frequent occurrence in engineering practice ; and, further, that by the aid of a simple device, it can easily be investigated in the laboratory.

The first problem is the ordinary one of a bar vibrating under the effect of its mass alone. The frequencies of the fundamental and harmonics are determined. The equation of the curve assumed at any instant by the elastic central line is obtained, and the positions of the nodes found.

When the bar vibrates under the influence of a longitudinal force in addition to its own mass, the problem is more difficult. The solution is exact up to a certain point, after which it is assumed that the longitudinal force is confined within certain limits. An approximate solution is then obtained which should be satisfactory for nearly all purposes.

Other portions of the paper deal with further cases of loaded and unloaded bars, both with and without longitudinal force. In each problem means are supplied by which the necessary magnitude of the constraining couple at the directed end can be found.

When the mass of a bar, in addition to that of a concentrated load, is taken into account, the method used is that of continuous approximation previously developed by the author. The method is found to be as readily applicable to this as to other cases.

In the last section an account is given of a few experiments on clamped-directed bars, and the results are seen to be in complete agreement with the theory. The paper

also contains the solutions of some cases of deflection under static loads.

A paper entitled "*On the Resistance of a Conductor of Uniform Thickness whose Breadth suddenly changes, and on the Shape of the Stream-lines*," was read by Prof. C. H. Lees.

A knowledge of the resistance of a conductor whose section suddenly changes is of considerable practical importance, but mathematical difficulties have prevented an exact solution of the problem. Lord Rayleigh has given an approximate solution of the case in which a cylinder of circular section is joined at one end to the plane surface of a large conducting solid; and Prof. Hicks has solved the case of a wire of small diameter ending in the surface of a conducting sphere. The mathematical difficulties of the problem disappear if the conductors are of rectangular section and one dimension; *e.g.*, the thickness remains constant, while the breadth suddenly changes and the two are joined together either with their axes or with two sides collinear. The paper shows that the resistance between two transverse sections through points situated at considerable distance from the change of section on opposite sides of it is equal to the sum of the resistances of the portions of conductor between each of the two sections and the change of section, each considered as part of an infinite length, plus the resistance of a length of either conductor equal to its breadth multiplied by an expression given.

Dr. Russell congratulated the author on having obtained the exact solution of an important problem, and thanked him for giving it in a form in which it could be utilised readily by electricians. Somewhat similar problems are of frequent occurrence in practice; in particular he instanced the measurement of the resistance of the bonds connecting the rails in electric tramway systems. The difficulty in this case is in knowing where the rail ends and the bond begins.

A small variation in the position of the potential contacts makes a large variation in the reading of the galvanometer. In many cases the only way of attacking the problem is to calculate the resistance from the known resistivity of the metals by the approximate method indicated by Maxwell. An exact solution, therefore, like the one obtained by the author, would be of great value in checking the accuracy of the approximate method.

A paper on "*The Inductance of Two Parallel Wires*" was read by Dr. J. W. Nicholson.

When direct and return currents flow in two wires of great length, and the alternation is not rapid, the effective self-induction per unit length of the system may be calculated readily by simple integration. If the wires have radii a, b, and permeabilities μ, ν, and if C be the distance between their axes,—

$$L = 2 \log c^2/ab + \tfrac{1}{2}(\mu + \nu).$$

This formula is often of little practical use when the frequency of alternation is several thousands per second. Such frequencies are of constant use in practical work. For example, in the measurement of small inductances by Mr. Campbell's method it is necessary to employ long leads in order to keep them at some considerable distance from the bridge and other circuits. The self-induction of these leads must be small, and a calculation of its value is very desirable. The general case presents very great mathematical difficulty, but the solutions given in the paper appear to include most cases of practical utility. The mode of proof depends upon a transformation of a harmonic series containing the Bessel functions of type k_n finite at infinity to a similar series with respect to a new origin.

Mr. A. Campbell congratulated the author, and said it was often desirable when measuring self-inductances to check the results by calculation. The author's formulæ would be useful in finding the inductance of parallel leads, although this was best obtained experimentally as a separate experiment.

Dr. Russell said that it required considerable mathematical skill and great patience to attack this problem, and so he thanked the author for having obtained a solution sufficiently accurate for practical purposes. He pointed out that the formula would have to be used with caution at very high frequencies as the capacity current was then appreciable. He suggested to the author that he should compute the kinetic energy of the ions or electrified particles by the motion of which modern theory explains the phenomena of the electric current. It has hitherto been the custom to assume that the self-inductance of a current flowing in a circuit can be calculated by finding the magnetic energy only, and this is what Dr. Nicholson has done. If we accept modern theory, however, we must admit that part of the total energy of a current is due to the kinetic energy of the ions. To take this into account it is necessary to add the term $\Sigma mv^2/i^2$ to Dr. Nicholson's solutions, where m is the mass of an ion, v the mean velocity given to it by the electromotive force, and i the current. In the case of metallic conduction this term is in general negligible compared with those found by the author. In cases, however, where the current takes place through gases—as in vacuum tube lighting—the value of the correcting term is appreciable, owing to the high velocity of the electrified particles. In a paper to the Röntgen Society on the measurement of a current through an X-ray tube, Mr. Duddell recently described some very interesting phenomena which he had noticed during his difficult but very successful experiments. The speaker thought that probably some of these effects might be explained by taking into account the kinetic energy of the moving ions.

A paper by Dr. Barkla and Mr. Sadler on "*Homogeneous Secondary Radiation*" was read in abstract by the Secretary.

Two papers by Prof. Morton entitled "Note on the Amount of Water in a Cloud formed by Expansion of Moist Air," and "An Elementary Treatment of the Motion of a Charged Particle in a combined Electric and Magnetic Field," were taken as read.

NOTICES OF BOOKS.

The Patents and Designs Act, 1907. By James Roberts, Esq., and H. Fletcher Moulton, Esq. London: Butterworth and Co. 1907.

The object of this exposition of the Patents and Designs Act of 1907 is to help the reader to interpret the provisions of the new Act and to forecast its probable effects. The difficulties which are likely to arise owing to ambiguity or obscurity of wording are pointed out, and the references to typical cases and decisions throw light upon the working of the Act. In the introduction the most important changes in the law are summarised.

Développement et Progrès de la Fabrication du Malt pendant les Quarante Dernières Années. ("The Development and Progress of the Manufacture of Malt during the last Forty Years"). By Ed. Eckenstein. Paris: A. Hermann. 1908.

The evolution of the more scientific and labour-saving processes which have replaced or are replacing the primitive rule-of-thumb methods originally employed in malting is described in a somewhat partial spirit in this book. Continental methods are given much greater prominence than those adopted in England, and certain reforms and workers are picked out for special mention, perhaps above their deserts, while other investigators whose researches have been at least of equal value are neglected. However, the history of the development of pneumatic and mechanical malting is fully discussed, and as the author has had much varied experience in constructing modern machinery, he brings an intimate practical knowledge to bear upon his subject. The book includes a bibliography of works on brewing and malting, practically only French

and French translations of German books being comprised in the list. In addition a short review is given of questions concerning malt and malting which have been discussed in the *Osterreichische Zeitschrift für Bierbrauerei* during the period of which the book treats.

Nitrate Facts and Figures, 1908. By A. F. Brodie James, F.S.S. London: Fredc. C. Mathieson and Sons.

The annual publication of abstracts of the balance sheets of the principal Nitrate and Railway Companies gives the investing public some opportunity of acquiring knowledge which might otherwise be difficult to obtain. Statistics relating to capital, dividend, reserve, output, &c., are tabulated in these notes, and the routes of the nitrate railways with their proposed extensions are shown in three maps. In the preface the author calls attention to the risks which shareholders run if they do not do their utmost to obtain regular monthly advices concerning production and other details of the running of the company in which they are interested.

The Fundamental Conceptions of Chemistry. By Dr. S. M. Jörgensen. Translated by M. P. Appleby, B.A. London and Brighton: Society for Promoting Christian Knowledge. New York: E. S. Gorham. 1908.

A book of this small size with what appears to be a somewhat pretentious title at once arouses in the mind the questions whether it is likely to find readers who will benefit by the study of it, and whether it can be recommended to the student as better worth his perusal than selections from one of the many excellent treatises on chemistry which have gained a world-wide reputation, and which are to be obtained in all languages. On the whole these questions may be answered in the affirmative. The book deals rather with general ideas than with details, and the conceptions of physical chemistry are introduced early and are well explained. Experiments which illustrate fundamental principles, and which require only comparatively simple reagents and apparatus, are fully described, and the historical growth of the science is emphasised, every advance being connected with the name of some great chemist. The book may safely be put into the hands of beginners whose instruction wants supplementing, and they will find it both lucid and interesting to read.

Alkali Soils, Their Nature and Reclamation. By Frank T. Shutt, M.A. Ottawa: Department of Agriculture.

In this Bulletin an account is given of the composition and characteristics of white and black alkali incrustations upon the soils of countries in which the rainfall is deficient, and different methods of removing, or lessening the amounts of, the injurious constituents are explained. The subject is one which has more interest for the farmers of the North-West plains of Canada and British Columbia than for English agriculturists, to some of whom, however, an accumulation of saline matter in hot weather upon land with a sandy, porous subsoil is not unknown.

CORRESPONDENCE.

THE POTENTIAL ENERGY OF THE ELEMENTS.

To the Editor of the Chemical News.

Sir,—I have read with interest Mr. Daniel J. Rankin's paper on the above subject in the Chemical News for June 26th.

It is, however, not apparent from the paper how the values for the "potential energy of the elements" given in the table were originally calculated; I should be obliged if the author would kindly enlighten me upon this matter.—I am, &c.,

H. Stanley Redgrove.

The Polytechnic, Regent Street, W.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xli., No. 8, 1908.

Action of Chlormethylsulphate on Amino Groups.—J. Houben and Hans R. Arnold.—Methyl sulphate acts as a methylating agent on aminobenzoic acid, attaching itself to the amino group, and methyl sulphuric acid salts of methylamino acids are formed:—

$$C_6H_4(COOH).NH_2 + SO_4(CH_3)_2 = C_6H_4(COOH).NH.CH_3SO_4H.CH_3.$$

With chlormethylate sulphate the methyl sulphuric acid salt of a chlormethylamino acid might result, or the chlormethyl sulphuric acid salt of a methylamino acid:—

$$C_6H_4(COOH).NH_2 < \begin{matrix} CH_2Cl \\ SO_4.CH_3 \end{matrix},$$

$$C_6H_4(COOH).NH_2 < \begin{matrix} CH_3 \\ SO_4.CH_2Cl \end{matrix},$$

With water chlormethylsulphate gives methyl but not chlormethylsulphuric acid. Thus the chlormethyl group is probably more reactive than the methyl group. When chlormethylsulphate acts on the amino group the chlormethyl group is split off and introduced into the amino residue. Thus when anthranilic acid and chlormethylsulphate react in ethereal solution, a white precipitate, which possibly contains the salt of a chlormethylanthranilic acid, is formed. On warming hydrochloric acid is evolved, and the salt of methylene anthranilic acid is obtained. The free acid polymerises very rapidly. Methylanthranilic acid and chlormethylsulphate should yield chlordimethylanthranilic acid, but again polymerisation takes place, methylene-bis-methyldianthranilic acid being formed—$C_6H_4(COOH).N(CH_3).CH_2.(CH_3)N.C_6H_4.COOH$. Ammonia reacts with chlormethylsulphate, giving the hydrochloric acid salt of methylamine, ammonium sulphate, and hexamethylenetetramine. Amines react differently; thus diethylamine yields tetraethylmethylenediamine—

$$2(C_2H_5)_2NH + SO_4(CH_3)(CH_2Cl) = (C_2H_5)_2N.CH_2.N(C_2H_5)_2HCl + HSO_4.CH_3.$$

Action of Ammonia upon Phosphorus. Different Modifications of Phosphorus.—Alfred Stock.—Four varieties of phosphorus are known—the colourless, Schrötter's red variety, Hittorf's and Schenck's (light red). A black and a white modification have also been described. The last is undoubtedly not pure phosphorus, but contains water. The statements about black phosphorus are contradictory, and no definite conclusions can be drawn from them. However, Schenck's and the colourless variety undoubtedly darken in presence of ammonia. When liquid ammonia is allowed to stand with phosphorus at the ordinary temperature a slow reaction takes place. The liquid reddens and the phosphorus darkens, while a black mass is deposited. When warmed the red liquid and the black substance are formed more quickly, and above 85° the liquid becomes colourless. At 90° to 100° the molten phosphorus is changed into a black mass which has no further action upon ammonia, although it consists chiefly of unchanged phosphorus. The residue on evaporating off the ammonia was treated with carbon disulphide and filtered. It amounted to 25 to 75 per cent of the phosphorus used. It contained 74 to 81 per cent of phosphorus, 2 to 3 per cent of nitrogen, 1 per cent of hydrogen. By treatment of the black substance with aqueous acids a red substance was obtained which had approximately the composition of the suboxide P_4O. Probably, however, the so-called suboxide is not a single substance, and it appears to contain always 1 per cent of hydrogen. The red substance

when heated to 470° yielded a residue which consisted of phosphorus nitride. It reacted in the cold with ammonia, turning black. The chief effect of the action of ammonia upon phosphorus appears to be the conversion of the colourless modification into a red variety which is identical with Schenck's. Thus, exclusive of colourless phosphorus, the author believes that four modifications exist, and he thinks that certain elements can occur as isomeric molecules.

Compounds of Mercury Cyanide with Alkalis and with Nitric Acid.—K. A. Hofmann and H. Wagner.—Mercury cyanide readily forms crystalline compounds with caustic potash. From determinations of the freezing-point, conductivity, and saponification it is evident that the complex ions $HgC_2N_2.\overline{O}H$ are formed, and when the concentration is sufficient they give solid salts $HgC_2N_2.HOK + H_2O$, $HgC_2N_2.HONa + H_2O$. From a solution of mercury cyanide in strong nitric acid a crystalline product, $[Hg(CN)_2]_2NO_3H$, can be obtained. It explodes on heating, and the aqueous solution has a strong acid reaction.

Preparation of Benzilic Acid.—Hans v. Liebig.—Large quantities of benzilic acid free from benzoic acid can be prepared by dissolving equal weights of benzile and caustic potash in twice the weight of water, and adding alcohol. The vessel is then heated on the water-bath to boiling for ten to twelve minutes, and the contents are turned into a beaker. The crystalline mass is drawn off after some hours. dissolved in cold water, and dilute sulphuric acid is added to the filtered solution, when benzilic acid separates out.

Action of Alkalis on Ethyl Sodium Thiosulphate.—A. Gutmann.—Alcoholic potash gives with ethyl sodium thiosulphate a white crystalline precipitate of sulphite and an alcoholic liquid, which smells strongly of mercaptan when water is added. Possibly the reaction occurs according to the equation $SO_2(ONa).SC_2H_5 + KOH = SO_3NaK + (C_2H_5)SOH$, and the substance $(C_2H_5)SOH$ is a thioethylhydroperoxide. The oxygen in it is very loosely bound, and it may have the formula $C_2H_5.\overset{II.}{S}.\overset{IV.}{O}.H$ or $C_2H_5.\overset{IV.}{S}\vdots O.H$ corresponding to ethylhydro-peroxide $C_2H_5.\overset{IV.}{O}\vdots O.H$ or $C_2H_5.\overset{IV.}{S}.H$ ($\ddot{O}$) corresponding to the sulphoxides $C_2H_5.\overset{\ddot{O}}{S}.C_2H_5$.

Oxidation of Brucine and Strychnine.—Hermann Leuchs. — Brucine and strychnine can be oxidised by potassium permanganate in acetone solution, and the products are crystalline acids. By cautious oxidation from both alkaloids a much smaller yield of a second alkaloid can be obtained. The formula of the first acid from brucine, brucinonic acid, is $C_{23}H_{24}O_8N_2$, and that of the acid from strychnine, strychninonic acid, is $C_{21}H_{20}O_6N_2$. Thus they differ from the corresponding alkaloid by an additional O_4, while H_2 less is present. The oxygen forms two carboxyl groups, possibly causing the breakdown of a carbon double bond, $\overset{H}{\underset{}{-C}}=\overset{H}{\underset{}{C}}-$. One of the carboxyl groups in the acid is neutralised by the basic nitrogen, while the other gives the compound its strongly acid character. The acids thus yield two kinds of esters —neutral mono-esters and basic diesters. As regards the hydrogen which is removed, probably a $>C<^{H}_{OH}$ group is transformed into a keto group. It is already known that in brucine and strychnine one oxygen atom is present in the form of acid amide group, $>N-CO$, and two more atoms in brucine form part of methoxy groups. The remaining atom is probably present in a secondary alcohol group, and thus the acids formed by oxidation must be ketone acids. The second acids produced by the oxidation are probably dihydro acids of formulæ $C_{23}H_{26}O_8N_2$ and $C_{21}H_{22}O_6N_2$ respectively. They contain two carboxyls and an alcohol group instead of a ketone group.

MISCELLANEOUS.

Geological Survey on the Coals of South Wales.—The Board of Agriculture and Fisheries desire to give notice of the publication of a Memoir of the Geological Survey on the Coals of South Wales. This Memoir gives the results of an investigation into the characters of the coals of South Wales, which was commenced in 1901. It includes not only the analyses which were made for the purposes of the investigation, but all previous analyses of recognisable seams, on which reliance can be placed, the total number amounting to 203. The sequence of the seams and their correlation throughout the coal-field is given, and the methods used in analysis of coal and the accuracy of coal analyses are discussed. The variations in seams, and in different parts of seams, are shown by a table, and the various classifications of coals are given. The volume is accompanied by ten plates illustrative of the sequence of seams, the distribution of different classes of coal, &c., several plates giving the positions of iso-anthracitic lines throughout the coal-field for certain seams or groups of seams. The anthracitic quality of the coals in a part of the coal-field is shown to have been in the main an original character and not the result of alteration. Copies may be obtained from any agents for the sale of Ordnance Survey maps, or directly or through any bookseller from the Ordnance Survey Office, Southampton, price 1s. 6d.

Royal Society of Arts.—The Annual General Meeting of the Royal Society of Arts was held on the 24th ult., Sir Steuart Colvin Bayley, K.C.S.I., C.I.E., Chairman of Council, in the chair. The business of the meeting was the reading the Report of the Council on the work of the Society during the past Session, the 154th since the formation of the Society in 1754. The Report, after a reference to the grant by His Majesty of permission to add the term Royal to the Society's title, gave a summarised account of the various papers read and lectures delivered during the past year. In referring to the award of the Albert Medal to Sir James Dewar for his Low Temperature investigations, special stress was laid on the power placed at the disposal of those interested in industrial applications of Science by the provision of temperatures so far below any hitherto available, and it was suggested that before long this new power would find numerous practical applications. Amongst the lectures delivered under the various Trusts available for such purposes, the course of lectures on Industrial Hygiene, provided out of funds left some years ago to the Society by Mr. Benjamin Shaw, was one of the most important. The award of a Medal, under the same Trust, to Professor W. Galloway, for his researches into the action of Coal Dust in Colliery Explosions, was also recorded. The number of papers worked at the examinations of the Society, just concluded, was well over 25,000, the highest number yet reached. The election of His Majesty the German Emperor, on the occasion of his visit to the country last year, as an Honorary Royal Member, was mentioned, as was also the death of two other Honorary Royal Members of the Society—the King of Sweden and the King of Portugal—during the year. At the conclusion of the reading of the Report, the result of the ballot for the election of the new Council was announced. His Royal Highness the Prince of Wales continues to hold the office of President, which he has filled since the accession of His Majesty in 1901.

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ACTION OF SELENIUM AND TELLURIUM ON ARSINE AND STIBINE.*

By FRANCIS JONES, M.Sc., F.R.S.E.

IN a paper on stibine, read before the Chemical Society and published in the *Journ. Chem. Soc.* for 1876, p. 641, I pointed out that sulphur decomposes the gas in presence of light, with formation of hydrogen sulphide and antimony trisulphide which deposits on the sulphur. Further, that the liberated hydrogen sulphide also reacts with stibine, producing antimony trisulphide and free hydrogen : — (*a*) $2SbH_3 + 6S = Sb_2S_3 + 3H_2S$; (*b*) $2SbH_3 + 3H_2S = Sb_2S_3 + 12H$. It was shown that the reaction serves as an extremely delicate test for stibine, and it was also used to determine its composition, by estimating the amount of antimony deposited as sulphide on the sulphur, as compared with the amount of hydrogen in the hydrogen sulphide evolved. The value of this method for determining the composition of certain hydrides has since been shown by its application to the case of germanium hydride, which is also decomposed by sulphur (Uber Germaniumwasserstoff, von E. Voegelen, *Zeit. Anorg. Chemie*, xxx., p. 325).

I also showed that sulphur acts similarly on phosphine and arsine, but not so readily as in the case of stibine.

It appeared probable that the elements selenium and tellurium, which are analogous to sulphur, would act in a similar way with arsine and stibine, and I have now to record the results of experiments made to decide this question.

In the course of these experiments it was necessary to have distinguishing tests for the hydrides of sulphur, selenium, and tellurium, which are so alike in their reactions. Each of these hydrides produces on paper moistened with solution of lead acetate, dark stains which are extremely similar, and I was unable to find any tests recorded which would serve to distinguish them. On trying the effect of various reagents upon these stains I found that hydrogen dioxide and hydrochloric acid were useful for this purpose, at all events in the case of a distinct stain. The differences in the behaviour of these stains with reagents are shown in the following table :—

Stain.	H_2O_2.	HCl (dilute).	HCl (strong).
Lead sulphide	Stain rapidly fades and leaves paper white.	Stain fades almost instantly and leaves paper white.	Stain instantly fades and leaves paper white.
Lead selenide	Stain slowly fades and leaves orange coloured stain (selenium).	Stain slowly fades and leaves orange coloured stain	Stain slowly fades and leaves orange coloured stain.
Lead telluride	Stain fades in course of time.	Stain fades only slightly and leaves greyish black stain.	Stain fades only slightly and leaves greyish black stain.

These reactions were employed to discriminate between the lead stains obtained in the course of the experiments, except in those in which arsine was used, as this gas acts directly on solutions of lead and produces stains on paper moistened with lead acetate very similar to the others. This reaction will be referred to subsequently.

Action of Selenium on Arsine.

(*a*) *In Sunlight.*—The arsine employed was generated in the way described in the paper already referred to ; that is to say, a solution of arsenious acid in dilute hydrochloric acid was allowed to drop from a stoppered funnel tube into a gas-bottle filled with pure granulated zinc. The exit-tube from the gas-bottle passed to a wash-bottle containing dilute soda, and the exit-tube from this passed to a drying tube filled with calcium chloride. The gas so obtained then passed into a tube containing powdered selenium exposed to sunlight. Under these circumstances the selenium became slowly coated with a deposit of arsenic selenide, arsenic being easily detected in the contents of the tube.

A reaction exactly similar to that occurring when arsine is passed over sulphur exposed to light therefore takes place, although more slowly :—$2AsH_3 + 6Se = As_2Se_3 + 3H_2Se$. Just as in the sulphur experiments, a secondary reaction was found to take place between the liberated hydrogen sulphide and the arsine, resulting in the formation of arsenic sulphide (which deposited on the glass tube) and free hydrogen, so in the selenium experiment, after prolonged exposure to sunlight, the glass tube was found slightly coated with arsenic selenide, due to the reaction of the liberated hydrogen selenide on the arsine :— $2AsH_3 + 3H_2Se = As_2Se_3 + 12H$.

(*b*) *At a Temperature of* 100° C.—Arsine was passed over selenium contained in a U-tube which was immersed in boiling water, and the whole apparatus was screened from daylight. There was no difference in the appearance of the tube at the conclusion of the experiment, and on testing the contents the absence of arsenic was proved, so that arsine is not decomposed by selenium at the temperature of boiling water.

(*c*) *In the Dark.*—Arsine was passed over selenium contained in a tube screened from light. The gas was passed for several hours, but no reaction occurred.

Action of Tellurium on Arsine.

(*a*) *In Sunlight*—Arsine was passed for three hours over powdered tellurium contained in a straight glass tube. At the end of the experiment there was no visible change in the appearance of the tellurium, but on removing it from the tube and heating it in a test-tube, a sublimate formed which, under the microscope, was seen to consist of distinct octahedral crystals. These were dissolved in water, hydrochloric acid and sulphuretted hydrogen were added, and a yellow precipitate of arsenic tri-sulphide appeared. So that, in presence of sunlight, tellurium decomposes arsine.

(*b*) *At a Temperature of* 100° C.—Arsine was passed over powdered tellurium contained in a U-tube protected from light and kept at a temperature of 100° C. After more than three hours treatment the action was stopped and the contents of the tube tested for arsenic as in the preceding experiment, but not a trace of arsenic was detected.

(*c*) *In the Dark.*—The experiment was repeated at the ordinary temperature for the same length of time, but no arsenic could be detected in the contents of the tube.

Action of Selenium on Stibine.

(*a*) *In Sunlight.*—Stibine, prepared in a similar manner to arsine as above, was passed over powdered selenium contained in a glass tube exposed to sunlight. The escaping gas was passed over paper moistened with solution of lead acetate. This very soon blackened, and the stains produced were not rapidly removed either by hydrogen dioxide or hydrochloric acid, and after a time they became orange coloured owing to separation of selenium. During the experiment it was noticed that a brown film slowly formed on the glass tube containing the

* A Paper read before the Manchester Literary and Philosophical Society, March 10, 1908. From the *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, liii., No. 12.

selenium, showing that in this case also a secondary reaction occurred between the liberated hydrogen selenide and the stibine :—$2SbH_3 + 3H_2Se = Sb_2Se_3 + 12H$.

(*b*) *At a Temperature of* 100° C.—Stibine was then passed over powdered selenium contained in a U-tube immersed in boiling water and screened from light.

As the selenium melts so readily that it might stop the passage of the gas, small portions were placed in the U-tube, separated by plugs of cotton-wool. At the exit a tube was placed containing paper moistened with solution of lead acetate. Soon after the experiment began the lead paper became stained, and eventually was blackened all over. The stains were not removed by treatment with either hydrogen dioxide or hydrochloric acid, so that selenium decomposes stibine at the temperature of boiling water.

(*c*) *In the Dark.*—Stibine was passed over powdered tellurium contained in a straight glass tube and screened from light. A paper moistened with lead acetate solution was placed between the stibine apparatus and the selenium tube, and another at the exit of the apparatus. When the gas had passed for half-an-hour the first paper was quite unaltered, but the second was stained half its length. The experiment was continued and ultimately the second paper was blackened all over. The stains were not removed by hydrochloric acid, so that, even in the dark, stibine is decomposed by selenium. This reaction was so remarkable and unexpected that the experiment was several times repeated with the same result. Of all the hydrides examined in contact with sulphur, selenium, and tellurium, stibine is the only one to be decomposed in the dark at the ordinary temperature, and then only when in contact with selenium.

Action of Tellurium on Stibine.

(*a*) *In Sunlight.*—Stibine was passed over powdered tellurium contained in a straight glass tube and exposed to sunlight. The exit tube contained a paper moistened with solution of lead acetate. This paper became darkened after the prolonged action of the gas, and the stains were not removed when placed in hydrochloric acid, so that stibine is slowly decomposed in presence of tellurium exposed to sunlight.

(*b*) *At a Temperature of* 100° C.—When stibine was passed over tellurium kept at a temperature of 100° C., the lead paper was distinctly stained after the prolonged passage of the gas, and the stains were not removed by hydrochloric acid.

(*c*) *In the Dark.*—In a similar manner, stibine was passed over tellurium, but in the dark and at the ordinary temperature no reaction took place.

The results of the investigation, including those of the previous paper in which sulphur was used, may be tabulated as follows (see next column).

In the previous paper I pointed out that the facility of the decomposition of the hydrides of phosphorus, arsenic, and antimony by means of sulphur when exposed to light, increased with the rise in the molecular weight of these gases, phosphine being very slowly decomposed, arsine more rapidly, and stibine very rapidly. Similarly, it is now to be noted that the action of these hydrides on sulphur, selenium, and tellurium corresponds with the rise in the atomic weights of these elements. This is shown by the comparative rapidity with which the action takes place in each case, stibine being readily decomposed by selenium and more slowly by tellurium exposed to sunlight, whereas arsine reacts on selenium slowly and on tellurium only very slowly. The fact that stibine is decomposed by selenium, even in the dark, is of course a marked exception. I have previously shown that paper coated with sulphur when in contact with stibine and exposed to light, may be used like sensitive paper in photographic printing, the exposed portions becoming orange coloured owing to the deposition of antimony trisulphide, the protected parts retaining the yellow colour of the sulphur. In a similar way paper coated with selenium and kept in contact with stibine may be used as printing paper, but there is, of course, not so great a contrast between the colour of the antimony selenide deposited and the selenium, as there is between the orange-coloured antimony trisulphide and the sulphur.

Element.	Hydride.	Result.
In Sunlight.		
Sulphur	AsH_3	Reacts slowly.
Selenium	AsH_3	Reacts.
Tellurium	AsH_3	Reacts.
Sulphur	SbH_3	Reacts easily.
Selenium	SbH_3	Reacts easily.
Tellurium	SbH_3	Reacts.
At 100° C.		
Sulphur	AsH_3	Reacts slowly.
Selenium	AsH_3	No action.
Tellurium	AsH_3	No action.
Sulphur	SbH_3	Reacts slowly.
Selenium	SbH_3	Reacts slowly.
Tellurium	SbH_3	Reacts very slowly.
In the Dark.		
Sulphur	AsH_3	No action.
Selenium	AsH_3	No action.
Tellurium	AsH_3	No action.
Sulphur	SbH_3	No action.
Selenium	SbH_3	Reacts.
Tellurium	SbH_3	No action.

Action of Arsine on Solutions of Lead.

I have already referred to the action of arsine on solution of lead acetate as preventing the adoption of the lead paper test with this gas. It is surprising that this reaction seems hitherto to have escaped observation, seeing how thoroughly the behaviour of both arsine and stibine with reagents has been investigated. In Gmelin's "Handbook," vol. iv., pages 268 and 335, it is stated on the authority of Simon that arsine and stibine do not act on lead acetate, and I have not found any other statement on the subject. In the course of the experiments above described I found in one case such a rapid blackening of the lead paper, that it occurred to me that it might be due to the arsine itself and not to any reaction on the selenium that was being exposed to it. This led me to remove the selenium tube and allow the gas to act on a fresh paper moistened with solution of lead acetate. This was rapidly darkened and the stain had very much the appearance of papers stained with lead selenide and telluride. These stains are distinguished from those due to lead selenide and telluride by not altering when treated with either strong or dilute hydrochloric acid.

On allowing arsine to bubble through solution of lead acetate contained in a wash-bottle, the liquid soon darkens in colour and a black precipitate separates. Subsequently a black shining mirror forms on the sides of the bottle and adheres firmly to the glass for some days, when it drops off.

I can find nothing in the precipitate but lead and arsenic, but on making quantitative determinations I found such varying proportions of the two elements in different preparations, that I could only conclude that the compound is probably an arsenide of lead but not of definite composition.

Similar experiments with stibine showed that this gas has no action on solution of lead acetate.

NEW APPLICATIONS OF ELECTRO-METALLURGICAL ALLOYS.*

By AD. JOUVE, Ingenieur-Conseil, Ancien preparateur de Chimie à l'Ecole Polytechnique, Directeur de la *Revue d'Electrochimie et d'Electrometallurgie.*

Among the alloys prepared by means of the electric furnace the most important are those containing iron, and particularly the ferro-silicons.

Substances prepared in this way have a percentage of silicon varying from 20 to 75 per cent, the most usual being 20 to 25, 50 to 55, and 70 to 75 per cent.

Their uses are well known to all metallurgists, while the analytical methods for determining them are very numerous, accurate, and wholly without complication, being all based on the solutions of the substance in alkalis in the presence of an oxidising agent such as peroxide of sodium, sodium oxide, or free oxygen.

It is a fact well known to analysts that no methods of analysis are based on the effect of acid, except in the case of hydrofluoric acid, and for this reason ferro-silicons with percentages above 20 per cent are insoluble in acids.

It is this peculiar property, due to silicon alone, which has been employed in an altogether unusual way; *i.e.*, instead of placing ferro-silicons in acids to dissolve them, acids during their preparation may be contained in ferro-silicon apparatus.

Thus, by using high percentage ferro-silicons, apparatus practically unaffected by acids is obtained.

Ferro-silicons are not, however, the only substances which possess this property. For, as this unalterability is due to the silicon, any alloy of a metal with this metalloid will behave in the same way to a greater or less degree according to the nature of the metal. It is evident, for instance, that calcium silicide will be unaffected by acid; the same phenomenon, in fact, occurs, for it is evidently much less affected than metallic calcium would be.

In answer to the question whether the problem of constructing apparatus for the preservation of acids is solved by making use of metallic silicides, it may be said that (1) these substances are very fragile; (2) they contract considerably on cooling, often breaking in the mould when scarcely solid and still at a bright red heat; (3) their melting-point is low compared with the temperatures occurring in ordinary foundry practice—*e.g.*, the second melting in a coke or furnace gas-heated cupola; and (4) certain of these compounds are powerful reducing agents, so that an effect similar to that produced by aluminium may occur. In consequence, fusion in the presence of the air necessary for combustion of the coke or furnace-gas is impossible without considerably lowering the percentage of silicon (especially in rich ferro-silicons—*i.e.*, about 35 per cent) to such a point that sometimes it will become as low as 15 per cent, and thus give alloys which are attacked by moderately strong acids.

Manufacture of Apparatus.—It is not proposed to enter here into complete details of the foundry methods employed, which belong rather to technical metallurgy, and it will simply be shown that by quite special and perfect arrangements, as well as by the correction of the mechanical properties with alloys of different natures, it has been possible to obtain, after six years' research, apparatus of all kinds and descriptions.

The first part of the process consists in obtaining melted metal suitable for pouring into moulds.

The simplest and most used of these methods consists in pouring alloys, melted in that apparatus, directly from the electric furnace into a mould lined with some refractory material. The mixture is then made. In a second method, the alloys obtained from the electric furnace are re-melted in an oil, or in certain cases in a crucible furnace and then cast into ingots.

Once the liquid metal is obtained, metals for corrective purposes are added. The number and nature of these is practically infinite for any particular case. They are added directly to the metal in the casting-ladle, usually with aluminium, which raises the temperature of the bath and increases the fluidity.

When the ladle is ready it is used mechanically, by a travelling crane, say, and carried quickly, to prevent cooling, to the mould. The pouring is effected by ordinary means without any special precautions.

The casting is removed as soon as it solidifies, is turned out into the warm casting sand, and thus annealed at a bright red heat. It is then ready for use.

Resistance to Acids.—The resistance of the metallic alloys of silicon, which have been called "Métillures," to acids is quite interesting, as the following examples will show. Nitric acid, even as a vapour, such as is obtained at the exit of a bisulphate retort or when mixed with nitrous acid, does not affect them at all. A striking example of this is given by a pipe which has been submitted for nearly five years to the daily passage of 660 lbs. of nitric acid vapour at temperatures varying from 150° to 200° without its loss in weight exceeding a few decigrms. in a total weight of a score of kilogrms. This loss occurred quite at the beginning of the period, and was probably due to a few impurities remaining on the inner surface of the pipe after fusion.

Sulphuric acid has still less effect, and acids of strength from 20 to 25, known as *petites eaux*, may be concentrated in vessels of this kind by direct heating and continuous evaporation.

Hydrochloric acid is analogous in its action, and use has been made of pipes of the above material for carrying and condensing its gases.

Acetic acid and the mixture produced by treating calcium acetate with sulphuric acid are without effect on "Métillures," even in the presence of air.

Resistance to other Reagents.—An important English firm has obtained the following figures relating to the resistance of "Métillures" to the action of cyanides, sulphocyanides, and prussic acid. The results are very remarkable, for they show both that the unattackability increases with the percentage of silicon, while for a suitable percentage it is practically negligible.

"Métillures" (20 per cent Nitric Acid).

No.	Weight in grms.	Change in weight. After 24 hours.	Reaction with sulphocyanide.
1.	6·4410	−0·0392	Violent.
2.	5·1669	−0·0047	Slight.
3.	8·1524	−0·0037	Moderate.
4.	14·5013	+0·0012	Moderate.
5.	1·7060	−0·0716	Very violent.
6.	1·4941	−0·0034	Very slight.
		After 48 hours.	
1.	6·4018	−0·0207	Violent.
2.	5·1622	−0·0006	Very slight.
3.	8·1487	−0·0032	Moderate.
4.	14·5025	+0·0045	Slight.
5.	1·6344	−0·0323	Violent.
6.	1·4907	−0·0007	None.

Métillures (13 per cent Sulphocyanide of Aniline).

No.	Weight in grms.	Change in weight. After 24 hours.	Reaction with potassium ferricyanide.
1.	6·3811	−0·0387	Very violent.
2.	5·1616	−0·0065	Moderate.
3.	8·1455	−0·0455	Violent.
4.	14·5070	+0·0055	Slight.
5.	1·6021	−0·0186	Violent.
6.	1·4900	−0·0160	Very slight.
		After 48 hours.	
1.	6·3430	−0·0675	Very violent.
2.	5·1551	−0·0219	Moderate.
3.	8·1000	−0·0433	Violent.
4.	14·5125	−0·0063	Slight.
5.	1·5835	−0·0216	Violent.
6.	1·4740	−0·0011	Very slight.

* A Paper read before the Faraday Society, June 23rd, 1908.

Under the same conditions, iron or any other metal in commercial use would be rapidly attacked, thus preventing its employment. The apparatus constructed up to the present time is extremely varied both in form and dimensions, ranging from evaporating dishes, troughs, right-angled bends, elbows, worms, ventilators, &c., and in the other from those weighing about 20 lbs. and having a diameter of 1 ft. to those weighing over one ton and measuring 7 ft. across, as well as pipes with a diameter of 8 ft. and weighing about three-quarters of a ton.

To sum up, it may be said that the production of a material capable of resisting acids is an accomplished industrial fact, and the principal desiderata are realised. It remains, however, to remedy the unmalleability of these substances. This question is actually being studied, and a solution seems probable in the near future.

As electro-metallurgists we may congratulate ourselves that without the electric furnace, which alone permits sufficiently high temperatures for the reduction of silicon or silicates by carbon to be obtained, the high percentage alloys of metals with silicon could not have been manufactured.

Further, without the electric furnace the fusion of high-percentage silicides would not have been possible. For when the percentage exceeds 50 the temperature of a coke or gas furnace is not sufficient to permit these alloys to be cast, not because they will not run, but because their specific heat is too low for the metal to be poured. In fact, it will not leave the crucible, but forms a pasty mass.

This latest conquest of the electric furnace has come at a most suitable time. For platinum, the most stable industrial metal, is becoming more and more rare, while its price is increasing by leaps and bounds, making its employment a matter of greater and greater difficulty.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

Part III.—Analysis of the Aluminium and Iron Groups, including Beryllium, Uranium, Vanadium, Titanium, Zirconium, and Thallium.

By ARTHUR A. NOYES, WILLIAM C. BRAY, and ELLWOOD B. SPEAR.

(Continued from p. 7).

General Discussion (continued).

6. The presence of beryllium does not involve any complication, since it goes with the aluminium in the process just referred to, and can be separated from it as described below. When, however, uranium and vanadium are to be provided for, this process is entirely inadequate, for upon the addition of ammonium hydroxide after acidifying, vanadium divides between the filtrate and precipitate wherever uranium is present, owing to the insolubility of uranyl vanadate; uranium itself will divide owing to the presence of H_2O_2 formed on acidifying the sodium peruranate solution; and vanadium, when present in large amount, again divides upon the addition of barium chloride to the acetic acid solution, owing to the slight solubility of barium vanadate; finally, vanadium interferes with the test for zinc with H_2S in acetic acid solution, since a precipitate of sulphur is always formed, and sometimes one of black vanadium sulphide. Moreover, the uranium precipitate obtained with ammonium hydroxide will, in general, be mixed with aluminium, beryllium, and vanadium, so that the difficult part of the separation still remains to be accomplished. After much experimenting, guided by the conception that under proper conditions of alkalinity it might be possible to separate the more basic elements, zinc, aluminium, and beryllium, from those present as constituents of acid radicals, chromium, uranium, and vanadium, it was finally found that this could be accomplished in a hot solution of sodium hydrogen carbonate, provided care be taken to prevent loss of carbon dioxide by heating the solution in an open vessel only to 90°, or better in a closed bottle to 100°. Under these conditions the separation is a fairly satisfactory one. A small amount of uranium may, however, be carried down almost completely when a large amount of aluminium or beryllium is present, making it necessary to test for uranium in the precipitate. Moreover, when uranium and vanadium are simultaneously present, each in large quantity (about 100 mgrms.) some uranyl vanadate precipitates, but a large quantity of both elements remains in the solution, so that their detection is not interfered with.

7. The separation of the zinc from the aluminium and beryllium in the precipitate is readily effected by dissolving it in hydrochloric acid, and adding a small excess of ammonium hydroxide. For the separation of the aluminium and beryllium from each other we studied what seemed to be the two most promising methods mentioned in the literature. The first of these was that described by Parsons and Barnes (*Journ. Am. Chem. Soc.*, 1906, xxviii., 1589), which consists in boiling for a short time a solution of the two elements to which enough sodium hydrogen carbonate is added to make a 10 per cent solution, whereby aluminium is precipitated and beryllium dissolved. We found, however, that though this method is satisfactory for the detection of beryllium when a moderate amount of aluminium is present, yet with a large quantity of aluminium (say, 100 to 500 mgrms.) 2 to 5 mgrms. of beryllium are almost completely retained in the precipitate, which may cause it to escape detection, and which at any rate leads to an incorrect estimate of its quantity. The second method investigated was that proposed by Havens (*Zeit. Anorg. Chem.*, 1898, xvi., 15), which consists in saturating a solution of the chlorides of the two elements in a mixture of ether and strong hydrochloric acid with hydrogen chloride gas, whereby aluminium is precipitated and beryllium remains in solution. It was found that this method gives entirely satisfactory results; even 0·5 mgrm. of aluminium is precipitated as $AlCl_3.6H_2O$, provided care be taken to use a sufficient proportion of ether and to saturate completely with the gas; even 100 mgrms. of beryllium remain wholly in solution, and 0·5 mgrm. is not carried out with a large quantity of aluminium. This method was therefore adopted for the separation, it being supplemented by a confirmatory test for beryllium based on the process of Parsons and Barnes.

8. The separation of the chromium, vanadium, and uranium, which are present together in the filtrate from the sodium hydrogen carbonate precipitate, also required much investigation. It was soon decided that there was more promise of effecting a separation of the first two of these elements in the state of chromate and vanadate, in which they already exist, than in a lower stage of oxidation; and it was found that the lead salts differed sufficiently in solubility in nitric acid to enable 0·5 mgrm. of chromium to precipitate while retaining 100 mgrms. of vanadium in solution. A separation based on this fact was therefore adopted. The excess of lead added is subsequently removed by saturating the filtrate with hydrogen sulphide. To avoid the addition and removal of lead when chromium is absent, a preliminary test for chromate with hydrogen peroxide is introduced. The uranium is separated from the vanadium (after oxidation to the vanadic state) by precipitating it as uranyl ammonium phosphate in acetic acid solution—a method that was found to give satisfactory results for the limiting case of a large proportion of uranium and a small proportion of vanadium, and also in the converse case. Vanadium is tested for by making the filtrate strongly alkaline with ammonia and saturating with hydrogen sulphide, whereby a violet-red solution of a vanadium sulpho-vanadate is formed.

9. We will next consider the analysis of the precipitate produced by sodium peroxide, which contains the manganese, iron, nickel, cobalt, thallium, titanium, and zirconium, the alkaline earth elements, and possibly phosphate. The main problems connected with this were the

* From the *Journal of the American Chemical Society*, xxx., No. 4.

separation of the manganese from the other elements, that of the alkaline earth elements from phosphate, and that of the titanium and zirconium from the iron and from each other.

10. In almost all schemes of qualitative analysis it is thought sufficient to test a portion of the precipitate for manganese by fusing it with sodium carbonate or by boiling it with lead dioxide and nitric acid, without isolating the manganese. These colour tests give, however, but little idea of the quantity of the element present. Moreover, aside from this objection, the large number of the elements contained in the precipitate in this scheme makes their separation necessary. The one reaction of manganese which seemed in every way suited for this purpose is that frequently employed in iron and steel analysis, consisting in the conversion of the manganese into the dioxide by the action of chloric acid and concentrated nitric acid. For this is not only a behaviour highly characteristic of this element, but, since the separation is carried out in a strongly acid solution, it might be anticipitated that the other elements, which are not oxidisable to insoluble peroxides, would not be retained in the precipitate to an important extent. Our experiments have shown that this is, in general, the case, but one exception has been discovered. It has been found, namely, that titanium, which is quadrivalent like manganese in the dioxide, when present even in considerable quantity (up to 50 mgrms.) may be completely precipitated with a large quantity of manganese (500 mgrms.), and that a large proportion, though not all of the zirconium is likewise carried down. The method is, however, otherwise so satisfactory that we have adopted it, special provision being made for this unusual case in a way that need not be described here. The procedure consists in dissolving the whole sodium peroxide precipitate in strong hydrochloric acid, in evaporating with excess of nitric acid, adding concentrated nitric acid and potassium chlorate, heating, and filtering off the manganese dioxide on an asbestos filter.

11. Owing to the fact mentioned above, that zinc is carried down in considerable quantity by manganese in the Na_2O_2 precipitation, experiments were made with the view of previously removing manganese by introducing this chloric acid procedure at the beginning of the analysis of this group. It was found, however, that vanadium, which is not carried down in the sodium peroxide procedure, is, like titanium, precipitated in large quantity with the manganese in the chloric acid procedure. It was found also that some zinc (1 to 4 mgrms.) may be carried down completely in the Na_2O_2 precipitate by iron, nickel, and cobalt, so that it would be still necessary to provide for the detection of zinc in the iron group. For these reasons, it is evidently best to have the sodium peroxide precipitation precede the treatment with chloric acid.

(To be continued).

Cæsium Dicalcium Sulphate.—J. D'Ans.—To prepare cæsium dicalcium sulphate a solution of gypsum is added to a solution of cæsium sulphate. The salt formed resembles the ammonium and rubidium salts when examined under the microscope. It does not crystallise with water and is very stable, and the stability increases as the temperature rises. The compounds of alkali sulphates with calcium sulphate which have been prepared have the following formulæ :—

$K_2Ca(SO_4)_2.H_2O$	$Rb_2Ca(SO_4)_2.H_2O$
	$Rb_2Ca_2(SO_4)_3$
$K_2Ca_5(SO_4)_6.H_2O$	
$(NH_4)_2Ca(SO_4)_2.H_2O$	
$(NH_4)_2Ca_2(SO_4)_3$	$Cs_2Ca_2(SO_4)_3$
$(NH_4)_2Ca_5(SO_4)_6.H_2O$	

As the atomic weight of the alkali sulphate increases the limits of the temperature of stability of the double sulphates become lower. Thus potassium syngenite is stable above 100°, rubidium syngenite only up to about 40°, ammonium dicalcium sulphate above 80°, and cæsium dicalcium sulphate below 0°.—*Berichte*, xli., No. 8.

THE CHEMICAL SOCIETY.

Proposal to Admit Women to the Fellowship.

The following correspondence has been forwarded to us for publication :—

1. *Copy of a Letter from the Secretaries to the Fellows of the Chemical Society.*

Burlington House, Piccadilly, W.,
June, 1908.

Dear Sir,—The Council of the Chemical Society have received a petition praying for an inquiry as to the views of the Society as a whole on the question of admitting women to the Fellowship.

Accordingly, the Council invite very careful consideration of the following brief statement of the chief arguments which have been used both for and against the admission of women.

It is proper to point out that the Council were advised on a former occasion by Counsel that there is some doubt whether, under the existing Charter, women are admissible as Fellows ; it is also well to remember that if admitted to this status, women would be eligible, like other Fellows, for a seat on the Council and to hold office.

Those who support the view that steps ought to be taken in order to provide for the admission of women to the Fellowship point out—

1. That the petition has been signed by 312 Fellows (including 10 Past Presidents, 12 Vice-Presidents, and 29 Members of Council, past and present), among whom are 33 Fellows of the Royal Society and the Professors of Chemistry or Heads of Chemical Departments of nearly all the most important Universities and Colleges in the country.

2. That a number of women are now devoting themselves to the science of chemistry, the study of which it is the chief object of the Chemical Society to promote. It is shown that they are capable of independent work by the facts stated in the petition : moreover, in the *Transactions* from January to May this year there are four papers by women authors independently of others in which they appear as joint authors.

3. The Chemical Societies of Berlin and America and the Institute of Chemistry admit women to full privileges of membership. The Chemical Society itself has placed the name of Madame Curie among those of its Honorary Members.

4. A small number of women chemists attend the meetings of the Society regularly as visitors, and no inconvenience has arisen from their presence. They ask that they should be admitted in order that, in addition to exercising the voting powers, they may use the Library and receive the publications of the Society on the same terms as Fellows ; at present they have to pay the higher price of publication charged to the general public.

5. The Society numbers over 2800 Fellows, while the number of women desiring admission at the present time is about 20 ; this number will probably increase as time goes on, but judging by the experience of other Societies, it is not likely greatly to exceed that number in the present generation. Should the number rise to as many as 50, their numerical strength would remain wholly insignificant in regard to the conduct of the Society's affairs ; consequently, any fear that female influence might hereafter dominate the Council, or even that one woman might be elected to the Council except only in recognition of her scientific ability, is not worth consideration. As to the undesirability of substituting one sex for another in offices of employment, little argument can be based on such a consideration so long as men continue to hold many of the teaching posts in women's colleges.

6. There is reason to believe that in the event of a decision in favour of applying for a supplemental Charter, the cost, or a large part of it, would be borne by the women chemists and their friends.

On the other hand, those who are unwilling to admit women to the Fellowship of the Chemical Society urge that—

1. The expense, probably amounting to several hundred pounds, which would be incurred by the Society if a supplemental Charter is necessary, is not justified by the small number of new Fellows likely to seek admission.

2. It may be gravely doubted whether the deliberate encouragement of women to enter the chemical profession would not operate unfavourably on women themselves in view of the arduous nature of chemical work.

3. Although it is true, as urged by supporters of the petition, that the number of women seeking admission is small, it is also claimed as a reason for admission that the volume of chemical work contributed by women is increasing rapidly. So long as the women who desire admission remain in such disproportionate minority, there will be an inevitable—although, of course, involuntary—tendency to overestimate their contribution to chemical knowledge and practice. An illustration of this principle may fairly be drawn from the petition itself, where figures are adduced to show that during the past thirty-five years women have been associated with 103 papers contributed to the *Transactions* of the Society, but it is not stated, though equally true, that while the total number of papers printed during that period exceeds 3400 only twenty-three are in the names of women alone.

4. Even assuming that these twenty-three contributions were independent of masculine inspiration, it may be questioned whether women have, as a group, shown marked aptitude for chemical pursuits, particularly when it is recalled that the authors in question have worked almost exclusively in collegiate institutions.

5. Moreover, by being welcomed as guests to the Society, women have been able to enjoy that chemical atmosphere and intercourse which Fellowship of the Society involves.

6. As regards the admission of Madame Curie to Honorary Membership, it must be borne in mind that Honorary and Foreign Members have no voting powers, and are not eligible for office.

7. Briefly stated, the position of those unfavourable to the admission of women is that, whilst gladly offering to those women who already have become chemists measures which would give them the benefits derived from attendance at the meetings, they deem it inexpedient publicly to encourage women to adopt chemistry as a professional pursuit, since such a course would tempt them into a career in which they may ultimately not find employment in view of the already over-crowded state of the profession.

Other minor considerations might be mentioned on both sides, and rejoinders to all the above statements are generally obvious. The Council therefore hope that every Fellow will carefully consider the arguments on both sides, and give them the weight which each, respectively, appears in his judgment to deserve.

You are requested, after making the necessary deletion, to return the enclosed ballot paper to the Secretaries in the accompanying envelope, which envelope must be endorsed with your signature. *Unsigned envelopes and signed ballot papers will be invalid.*

The ballot will close on the first day of October next. —We are, Sir, yours faithfully,

M. O. FORSTER,
ARTHUR W. CROSSLEY, } Hon. Secretaries.

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2. *Copy of a Letter from Past Presidents of the Chemical Society accompanying the communication of the Petition to the Fellows.*

Oxford, 1st July, 1908.

DEAR SIR,—In the letter, which has been sent by the Secretaries of the Chemical Society to every Fellow, on the question of admitting women to the Fellowship, reference is made to a petition received by the Council. We think it desirable that the petition itself, which is not only a petition but a declaration of opinion on the part of a large body of the Fellows of the Society, should be made known generally, together with the names of those by whom it was signed. Accordingly we enclose herewith a copy of the petition as presented to Members of the Council.

Before the issue of the voting papers the attention of the Secretaries was called to an ambiguity which is due to the introduction of the words "the full rights and privileges of." We suggest that those Fellows who are in favour of the admittance of women to the Fellowship, and not only to "the full rights and privileges of the Fellowship," should strike out these words. It would clearly be possible, however unreasonable, to create a class who, though not actually Fellows, were admitted to all the rights and privileges of the Fellowship. That such a class should be created is not the question which the Council were asked and consented to put.—We are, Sir, yours faithfully,

(Signed)

WILLIAM ODLING, T. E. THORPE,
WILLIAM CROOKES, J. EMERSON REYNOLDS,
A. VERNON HARCOURT, WILLIAM A. TILDEN,
HENRY E. ROSCOE, R. MELDOLA,
HUGO MÜLLER, ALEX. CRUM BROWN.
W. J. RUSSELL,

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3. *Copy of the Petition.*

TO THE PRESIDENT AND COUNCIL OF THE CHEMICAL SOCIETY.

GENTLEMEN,—We, the undersigned Fellows of the Chemical Society, being of opinion that the time has come when the Fellowship of the Society should be rendered accessible to women, request the Council to take such steps as may appear desirable to ascertain the wishes of the Society as a whole in regard to this question.

We understand that there is now an appreciable and increasing number of women of University training engaged in advanced teaching, and in original investigation in chemistry, who desire admission to the privileges of the Fellowship, and as the Chemical Society was founded for the advancement of Science, it seems to us neither just nor expedient that a body of highly qualified workers should be excluded solely by reason of sex.

From the following table, compiled from the Society's journal of the past thirty-five years, it will be seen that the number of papers contributed either alone, or jointly, by women is increasing rapidly:—

	Number of Papers published in—	
	Proceedings.	Transactions.
1873—82..	2	2
1883—92..	7	7
1893—02..	45	33
1903—07..	66	61

We may further point out that not only have women contributed original memoirs to these publications, but they have rendered valuable service to the Society as abstractors and in the compilation of the Indexes.

As is well known, the Chemical Societies of Berlin and America, the Society of Chemical Industry, and the Faraday Society admit women on the same terms as men, and our Society has found a place for Madame Curie among the Honorary and Foreign Members; we consider, therefore, that the restriction should be removed under which the Chemical Society denies to women chemists the advantages extended to them by the sister Societies at home and abroad.—We are, Gentlemen, your obedient servants,

(Signed)

Robt. T. Abell, R. H. Adie, John Allan, Albert E. Andrews, A. Angel, Paul S. Arup, P. C. Austin, G. H. Bailey, H. B. Baker, Horatio Ballantyne, Edward C. Cyril Baly, George Barger, Wm. Barlow,

M. Barrowcliff, P. Phillips Bedson, W. H. Bentley, Leslie H. Berry, Edward Bevan, Geo. S. Blake, Bertram Blount, B. H. Bowles, H. L. Bowman, Joseph Brierley, James S. Broome, Alex. Crum Brown, David Brown, William Burton, J. C. Cain, Kenneth Caldwell, Wm. Caldwell, Hugh C. H. Candy, H. C. H. Carpenter, John A. Carpenter, Francis H. Carr, John Castell Evans, F. W. Caton, R. M. Caven, D. L. Chapman, A. H. Church, H. T. Clarke, G. W. Clough, J. Bernard Coleman, A. J. Cook, A. H. Coote, H. F. Coward, J. C. Crocker, Holland Crompton, William Crookes, C. F. Cross, J. K. Crow, Alfred V. Cunnington, W. A. Davis, H. M. Dawson, George Dean, William S. Denham, Cecil H. Desch, Edward Divers, George Dixon, Harold B. Dixon, Leonard Dobbin, F. W. Dootson, Thos. R. Duggan, Bernard Dyer, Lewis Eynon, T. W. Fagan, Thomas Fairley, E. H. Farr, Chas. A. Fawsitt, Charles E. Fawsitt, Ernest Feilmann, H. J. H. Fenton, Alex. Findlay, Horace Finnemore, W. W. Fisher, John Foggie, John S. Ford, Gilbert J. Fowler, J. J. Fox, Francis Francis, H. Frankland, Percy F. Frankland, Angus Fraser, Robt. C. Gale, Edward Gardner, J. A. Gardner, G. H. Gemmell, C. S. Gibson, John Gibson, J. F. H. Gilbard, J. N. Goldsmith, F. Gossling, Jas. Grant, R. W. Gray, Thomas Gray, A. G. Green, A. J. Greenaway, Robt. G. Grimwood, P. Haas, A. D. Hall, W. A. Handcock, F. W. Harbord, A. Vernon Harcourt, Arthur Harden, H. Harding, E. F. Harrison, Fred T. Harry, W. Beaumont Hart, E. G. J. Hartley, H. B. Hartley, W. N. Hartley, Jack V. J. Hayman, Otto Hehner, G. G. Henderson, James Hendrick, J. T. Hewitt, T. P. Hilditch, W. R. Hodgkinson, George T. Holloway, Alfred Holt, jun., E. Grant Hooper, F. G. Hopkins, Edward Horton, Alfred G. Howard, Jul. Hübner, A. K. Huntington, G. Nevill Huntly, W. H. Hurtley, A. Hutchinson, Ernest W. Jackson, Herbert Jackson, T. Campbell James, F. R. Japp, E. Jones, Francis Jones, H. O. Jones, A. M. Kellas, M. Kemp-Welch, Frank E. King, Frank W. G. King, J. Falconer King, F. Stanley Kipping, Patrick H. Kirkaldy, Harley F. Knight, W. R. Simpson Ladell, F. E. E. Lamplough, G. Druce Lander, Arthur Lapworth, A. T. Larter, R. T. Lattey, Alexander Lauder, H. D. Law, J. B. Leathes, Frederic H. Lees, R. Lessing, Edward W. Lewis, W. J. Lewis, J. Lewkowitsch, Arthur R. Ling, G. D. Liveing, J. P. Longstaff, T. M. Lowry, W. Lowson, G. Roche Lynch, John S. MacArthur, Hamilton McCombie, Alex. McKenzie, John E. Mackenzie, Herbert McLeod, Alan Macmullen, W. Maitland, Arthur Marshall, Hugh Marshall, N. H. Martin, F. E. Matthews, Raphael Meldola, A. M. Meldrum, A. E. Middleton, Henry A. Miers, J. Bruce Miller, Edmund J. Mills, W. H. Mills, Chas. W. Moore, T. S. Moore, Hy. Forster Morley, Richard J. Moss, A. de Mouilpied, Hugo Müller, M. M. Pattison Muir, Thos. J. Murray, D. H. Nagel, S. S. Napper, F. H. Neville, B. E. R. Newlands, W. E. Oakden, A. O'Farrelly, Kennedy J. P. Orton, John Parkin, S. Parrish, T. S. Patterson, S. J. Peachey, F. Mollwo Perkin, W. H. Perkin, W. H. Perkins, E. P. Perman, James C. Philip, G. S. Philpotts, Robert H. Pickard, Sam. S. Pickles, D. R. Pinnock, George P. Pollitt, James H. Pollok, W. J. Pope, F. B. Power, Henry R. Proctor, C. Proctor, Thomas Purdie, Frank Lee Pyman, J. E. Purvis, G. G. Quinn, L. G. Radcliffe, A. A. Read, Walter F. Reid, P. Remfrey, J. Emerson Reynolds, Wm. C. Reynolds, Edmund M. Rich, F. G. Richards, H. D. Richmond, J. H. Robbins, James Roberts, junr., Wm. Robertson, Henry H. Robinson, R. Rodger, Harold Rogerson, Henry E. Roscoe, S. Rubemann, A. R. Runeckles, E. J. Russell, W. J. Russell, J. H. Ryffel, Alfred Gordon Salamon, A. H. Salway, Henry J. S. Sand, H. C. Sayer, S. B. Schryver, W. J. Sell, George Senter, A. Humboldt Sexton, W. B. Shaw, W. F. J. Shepheard, N. V. Sidgwick, J. L. Simonsen, F. S. Sinnalt, Sidney Skinner, Arthur Slator, Samuel Smiles, Clarence Smith, Norman Smith, Arthur Smithells, Frederick Soddy, J. F. Spencer, F. E. Stead, Jas. Steger, T. Stenhouse, Thos. Stevenson, A. W. Stewart, F. Henry Streatfeild, R. de Fleming Struthers, Geo. Stubbs, J. J. Sudborough, R. R. Tatlock, R. L. Taylor, W. H. Taylor, F. Thomas, Claude M. Thompson, John Millar Thomson, R. T. Thomson, Leonard Temple Thorne, J. F. Thorpe, T. E. Thorpe, Thomas Tickle, W. A. Tilden, C. K. Tinkler, F. D. Toyne, Frank Tutin, Thos. Tyrer, V. H. Veley, E. W. Voelcker, John Wade, A. F. Walden, James Walker, George Stanley Walpole, George J. Ward, H. Edmeston Watson, J. Adam Watson, H. E. Watt, John Watts, Emil A. Werner, E. Wheeler, R. Whymper, W. H. Willcox, W. Williamson, N. T. M. Wilsmore, Leonard P. Wilson, T. B. Wood, J. Woodward, H. Wren, W. Palmer Wynne, Jos. Yates, George Young, J. Rymer Young, Sydney Young.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 18th, 1908.

Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

Messrs. F. W. Caton, H. F. Coward, and E. J. Watkins were formally admitted Fellows of the Society.

The President made a short communication with reference to the Seventh International Congress of Applied Chemistry, to be held in London at Whitsuntide, 1909 (May 27th to June 2nd), under the Hon. Presidency of Sir Henry Roscoe, he himself being the acting President. The King has consented to be Patron, and the Prince of Wales Vice-Patron; it is hoped that His Royal Highness will be able to open the Congress. The meetings will be held in the University Buildings, in the Imperial College of Science, and in the Central Technical College. There are special sections for (1) Analytical Chemistry; (2) Inorganic Chemistry and Allied Industries; (3) Metallurgy and Mining—Explosives; (4) Organic Chemistry and Allied Industries; (5) Industry and Chemistry of Sugar; (6) Starch Industry; (7) Agricultural Chemistry; (8) Hygiene, Medical, and Pharmaceutical Chemistry—Bromatology; (9) Photographic Chemistry; (10) Electrical and Physical Chemistry; and (11) Law, Political Economics, and Legislation with reference to Chemical Industries, of which Presidents, Vice-Presidents, and Secretaries have already been appointed.

A considerable sum has already been collected privately to meet the expense of the Congress, and a general appeal will be issued shortly. The provisional Programme of the week has been drawn up; it comprises the opening meeting in the Albert Hall, a conversazione at the Natural History Museum, a banquet at the Crystal Palace, and lectures by Prof. Haller, Prof. Otto Witt, Prof. Nasini, and Sir Boverton Redwood. Sectional meetings, at which papers will be read, will be held daily during the meeting. Committees have been formed in foreign countries to organise the work of the sections, and an executive Committee has charge of the arrangements at home. It is anticipitated that the Congress will be largely attended; meetings in Paris, Berlin, and Rome were attended by about 3000 chemists. The Hon. Secetary is Mr. William Macnab, of 10, Cromwell Cresent, S.W.

Certificates were read for the first time in favour of Messrs. William Colet Birch, B.A., 22, Glazbury Road, W. Kensington, W.; John Griffin, B.A., 7, Carlton Terrace, Batley; Joseph Albert Hughes, School of Mines, Charters Towers, Queensland; Thomas Ernest Hull, 6, Selborne Terrace, Greenbank Darlington; James Colquhoun Irvine, Ph.D., D.Sc., Dunmurry, Rathelpie, St. Andrews; Frederick Martin Kay Menzies, M.D., F.R.C.P., 79, Davies Street, Berkeley Square, W.; Howard Houlston Morgan, B.Sc., Technical College, Auckland, New Zealand.

A certificate has been authorised by the Council under By-law I. (Par. 3) in favour of H. V. Krishnayya, B.A., Mallesvaram, Bangalore, Mysore, India.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected :— William Henry Ballantyne, B.Sc.; Edward Morris Bevan; Donald Francis Blyther, B.Sc.; James Brown; Charles Duncan Cooper; John Robert Cowburn; James Hill Fairweather; Kaufman George Falk, B.Sc., Ph.D.; Frank William Crossley-Holland; Norman Holland; Henry Brougham Hutchinson, Ph.D; James Kirkman King, B.A.; Lionel Gordon Larmuth; Henry Robert Lyell; Alfred Ash Meggitt, B.Sc.; Stanley Allen Warrington Okell; Haradhan Ray, M.A.; William Readwin; Clement Thomas Rutter; James Edward Southcombe, M.Sc.; John Day Speed; Alexander Mackintosh Stewart; Edward Stokes, B.A.; Hari Prasad Vidyant, M.A.; Herbert Horace Ward; Charles Harold Wright, B.A.; Harry James Yates; Charles Robert Young, B.Sc.

Of the following papers, those marked * were read :—

"143. "*The Thermal Decomposition of Hydrocarbons.* Part I. [*Methane, Ethane, Ethylene, and Acetylene*]." By WILLIAM ARTHUR BONE and HUBERT FRANK COWARD.

The results of a systematic investigation of the modes of decomposition of the four hydrocarbons at temperatures between 500° and 1200° were described, The theories advanced by Berthelot, V. B. Lewes, and others were critically examined, and doubts raised as to the importance of acetylene as a factor in such processes.

Methane, which is by far the most stable of the four hydrocarbons, and a principal product of the decomposition of the other three, decomposes for the main part *directly* into carbon and hydrogen. The decomposition is, within the range of temperature investigated, a surface effect, and the carbon deposited is of a peculiarly hard and lustrous type. The large quantities of methane formed during the decomposition of the other three hydrocarbons can only be explained on the supposition that "residues," such as ⋮CH and :CH_2 (which may be considered to have a momentary separate existence during the dissolution process), are directly "hydrogenised" in an atmosphere rich in hydrogen. The assumption of the momentary formation of such "residues" (or the tendency to give rise to them, which actually becomes operative at moderately high temperatures) as the result of the initial dissolution of the hydrocarbon molecule, renders it possible to formulate a rational scheme of the chief causes at work, and their modes of operation in each particular case.

It may be supposed that these "residues" are capable of (*a*) forming $H_2C{:}CH_2$ or HC⋮CH as the result of encounters with other like residues, or (*b*) breaking down directly into carbon and hydrogen, or (*c*) combining with hydrogen to form methane, and that all three possibilities may be realised simultaneously in proportions dependent on the temperature and the amount of hydrogen present. The scheme of decomposition of the three hydrocarbons (omitting secondary "polymeric" changes, which are essentially low temperature effects) is as follows :—

$$\underset{\text{Ethane.}}{\overset{H\ H}{H\cdot\dot{C}\cdot\dot{C}\cdot H}} = [2(\dot{:}CH_2) + H_2] = \begin{cases} (a)\ C_2H_4 + H_2. \\ (b)\ 2C + 2H_2 + H_2. \\ (c)\ \textit{plus}\ H_2 = 2CH_4. \end{cases}$$

$$\underset{\text{Ethylene.}}{\overset{H\ H}{H\cdot\dot{C}{:}\dot{C}\cdot H}} = [2(\dot{:}CH) + H_2] = \begin{cases} (a)\ C_2H_2 + H_2. \\ (b)\ 2C + H_2 + H_2. \\ (c)\ \textit{plus}\ 2H_2 = 2CH_4. \end{cases}$$

$$\underset{\text{Acetylene}}{H\cdot C{:}CH} = [2(\dot{:}CH)] = \begin{cases} (b)\ 2C + H_2. \\ (c)\ \textit{plus}\ 3H_2 = 2CH_4. \end{cases}$$

Polymerisation to C_6H_6, &c.

DISCUSSION.

Prof. ARMSTRONG said that the conditions under which acetylene was produced were undoubtedly peculiar; he had sought for it in vain in the oil gas produced by cracking petroleum. If formed in the process, it underwent change very readily. It was by no means necessary to assume that the benzene which was produced was formed from acetylene. He could not agree with Dr. Bone as to the influence of surfaces in the changes studied; he thought they must play a predominant part. He was in agreement with him, however, as to the manner in which methane was formed; that is to say, that it was formed by the hydrogenation of fragments.

Dr. DIVERS asked whether the production of methane from acetylene at 800°, in presence of large excess of hydrogen, was not sufficiently accounted for as being the result of the union of the acetylene and hydrogen with decomposition of the product into methane, without making the assumption of the temporary existence of the substance CH ?

Prof. MILLS referred to the great importance of the author's investigation, especially in connection with the manufacture of coal-gas. He thought the experiments showed that hydrogen (probably on account of its less density) protected ready-made methane better than nitrogen did. Hydrocarbons, such as CH and CH_2, if they could possibly be formed, would, in his opinion, be certain to polymerise (like acetylene, for instance), and, in their polymerised state, it would be extremely unlikely that hydrogen would combine with them.

Prof. BONE, in reply, said he was clearly of the opinion that, whilst the decomposition of methane was, within the range of temperature investigated, entirely a surface effect, in the other three cases surface played a much less prominent part. No one, he thought, could witness the sudden decomposition of acetylene at high temperature with its accompaniment of incandescence without admitting that the chemical change took place throughout the whole mass of the gas and was not confined to the layer in contact with the hot walls of the containing vessel. Time did not permit him to cite all the evidence in favour of the hypothesis that such residues as :CH_2 and ⋮CH are actually formed during these decompositions; but he thought that when Dr. Divers and Prof. Mills had had the opportunity of studying the whole of the facts brought to light during the investigation, their doubts on that point would largely disappear. He himself felt convinced that, in the cases of ethane and ethylene, the collapse of the molecule was preceded by the elimination of hydrogen in the manner stated in the paper.

*144. "*The Rusting of Iron.*" By WILLIAM AUGUSTUS TILDEN.

An account was given of a series of experiments from which the following conclusions are drawn.

1. Oxygen or air together with liquid water are alone necessary to produce rusting without the assistance of carbonic acid, failure on the part of other experimenters to produce rusting in iron prepared by treatment with chromic acid being probably due to "passivity."

2. Water alone in the absence of oxygen attacks iron slowly, producing a film of what is probably ferrous hydroxide, as it is wholly converted into brown rust on admission of pure oxygen. In this connection, the experiments of Whitney (*Journ. Am. Chem. Soc.*, 1903, xxv., 298), repeated and approved by Walker, Cederholm, and Bent (*Journ. Am. Chem. Soc.*, 1907, xxix., 1255), were confirmed.

3. Iron rust even when very old and constantly exposed to the weather always contains ferrous oxide.

4. The process of rusting is due, in the first instance, to electrolytic action promoted in all ordinary cases by the existence of carbonic acid in water exposed to the air, and by the presence in iron of various compounds of carbon, silicon, phosphorus, and sulphur. That electrolytic action does occur locally in all commercial iron, whether malleable iron, grey or white cast-iron, or steel immersed in water, is shown by the use of the "ferroxyl" indicator (phenolphthalein and ferricyanide) introduced by Walker and his colleagues, and in other ways. In ordinary rusting, the process is also assisted by the depolarising action of the layer of ferric oxide or hydroxide formed externally on the rust spot.

The conditions of rusting of pure iron have never yet been studied, inasmuch as a pure iron in a massive form, if indeed in any form, is unknown.

Discussion.

Dr. Jowett said that he was interested to know that Prof. Tilden's experiments confirmed those carried out by himself many years ago. Although there were difficulties in the hydrogen peroxide theory of rusting, he would like to know how the electrolytic theory would account for the inhibiting effects of salts like sodium nitrite and potassium ferrocyanide, and the absence of this inhibiting effect by potassium nitrate and potassium ferricyanide, &c.

Prof. Armstrong said that as they were carried out in his laboratory, he had enjoyed the opportunity of witnessing all Dr. Moody's experiments. One of his most striking observations was that a piece of iron, insulated from the glass by coating the ends with paraffin-wax, had remained unrusted after many months' exposure partly immersed in water and partly in air, but on turning the tube so that the metal came into contact with the glass at some point, the iron soon rusted. It therefore did not seem to be in a passive state. He (the speaker) thought the effect was perhaps due to silicic acid from the glass.

But even admitting, for the sake of argument, that treatment with chromic acid had rendered the iron passive, Prof. Tilden's results, important and valuable as they were, did not, in the speaker's opinion, in the least invalidate Dr. Moody's conclusions. The subject must be considered from the theoretical as well as from the practical side. Recalling the fact that, in 1885, in the course of the discussion on Mr. Brereton Baker's communication on "Combustion in Dried Gases," he had insisted that the conditions to be satisfied in the case of any chemical change were those involved in a galvanic cell—that the system must contain an electrolyte—Prof. Armstrong said that this contention had been entirely justified by later observations, especially by Mr. Baker's work on the interaction of hydrogen and oxygen. Not only was a dry mixture of these gases inert, but the presence even of liquid water was not sufficient to determine interaction; dirty water—water containing impurity which rendered it an electrolyte—alone conditioned the change. From this point of view, it was impossible that interaction should set in between iron, water, and oxygen; some trace of acid impurity must be present to condition the change.

Prof. Tilden, in reply, recalled the familiar fact that water in contact with glass became alkaline and not acid, and that, although he could not profess to account for the effects produced by all the salts mentioned by Dr. Jowett, it was obvious that all those which, like alkalis, produced hydroxyl ions in aqueous solutions would tend to retard the process of rusting.

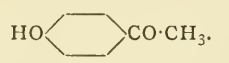
*145. "*Studies on Zirconium.*" By Edgar Wedekind and Samuel Judd Lewis.

The authors have studied the chemical and physical properties of zirconium. From a specimen containing 95·55 per cent of zirconium and 4·14 per cent of oxygen, the value 14 was obtained for the atomic volume and the values 6·078 and 6·753 for the atomic heat.

146. "*The Constituents of Canadian Hemp.* Part I. *Apocynin.*" By Horace Finnemore.

The principal constituent of the root of *Apocynum cannabinum* (0·2 per cent) is identical with the crystalline apocynin of commerce, and with the product previously isolated by Wood (*Journ. Am. Med. Assoc.*, 1904, xliii., 1953) for pharmacological purposes.

Apocynin, $C_9H_{10}O_3$, which has a faint odour of vanillin, forms slender colourless prisms, m. p. 115°. It is convertible into a crystalline *potassium* derivative, and into *acetyl*, *benzoyl*, and *methyl* derivatives, m. p. 57°, 106°, and 51° respectively; it yields an *oxime* and a well-defined *hydrazone* and *semicarbazone*, m. p. 126° and 167° respectively; its molecule contains a single methoxyl group. As it has no aldehydic properties, it follows that apocynin is a hydroxymethoxyacetophenone. It is, in fact, identical with the acetovanillone (4 - hydroxy - 3 - methoxyacetophenone) obtained by Tiemann (*Ber.*, 1891, xxiv., 2855), from *iso*eugenol, and by Goldschmiedt and Hemmelmayr (*Monatsh.*, 1894, xxxv., 338), from scoparin, and has the constitution (compare following abstract):—



The pharmacological properties of apocynin are under investigation. A synthesis of acetovanillone from vanillic acid by Neitzel (*Ber.*, 1891, xxiv., 2863) could not be confirmed, and another by T. Otto (*Ibid.*) gave a yield too small for practical use; the product, however, was identical with apocynin.

147. "*A New Synthesis of Apocynin.*" By Horace Finnemore.

The previously known syntheses of apocynin (acetovanillone) being unsatisfactory (preceding abstract), the author has synthesised this substance from vanillin by an application of the Grignard process. Benzoylvanillin, $C_6H_3(OBz)(OMe)\cdot CHO$, is converted by magnesium methiodide, with subsequent hydrolysis into *benzoylapocynol*, $MeO\cdot C_6H_3(OBz)\cdot CH(OH)\cdot CH_3$, m. p. 128°, the phenolic benzoyl derivative of the secondary alcohol corresponding with apocynin. This benzoyl compound is oxidised by chromic acid mixture to *benzoylapocynin*, $MeO\cdot C_6H_3(OBz)\cdot CO\cdot CH_3$, m. p. 106°, which gives on hydrolysis 4 - *hydroxy* - 3 - *methoxyacetophenone*, $MeO\cdot C_6H_3(OH)\cdot CO\cdot CH_3$, m. p. 115°; this is identical with natural apocynin, and with acetovanillone prepared from guaiacol (preceding abstract). The yields throughout are good.

Apocynol or 4-*hydroxy*-3-*methoxyphenylmethylcarbinol*, $MeO\cdot C_6H_3(OH)\cdot CH(OH)\cdot CH_3$, m. p. 101°, obtained by hydrolysing the above synthetic benzoyl derivative, may also be formed, although with poor yield, directly from apocynin by the action of sodium amalgam. This alcohol and the corresponding *dihydroxycarbinol*, $C_6H_3(OH)_2\cdot CH(OH)\cdot CH_3$, that is formed from it by the action of suitable hydrolytic agents, promise to be of interest pharmacologically by reason of their very close relation to adrenaline.

148. "*The Constitution of the Diazonium Perbromides.*" By Frederick Daniel Chattaway.

The view first suggested by Kekulé as an alternative and rejected by him, that the diazonium perbromides have the constitution $R\cdot NBr\cdot NBr_2$, that is, are tri-N-bromo-derivatives of the hydrazines, receives strong support from the fact that they are produced quantitatively when the required amounts of bromine are added to aromatic hydrazines dissolved in acetic acid.

The author has recently shown (*Trans.*, 1898, xciii., 852) that diazonium bromides are produced quantitatively by the action of bromine on the hydrazines, and has expressed the view that these compounds when in acid solution are really di-N-bromo-substituted hydrazines

which are produced from the hydrazines by a process of substitution exactly similar to that which occurs when other compounds containing hydrogen attached to nitrogen are submitted to the action of bromine.

According to this view, the production of diazonium perbromides thus is the final and completing step in the replacement of the hydrogen of the $-NH\cdot NH_2$ group by bromine, thus :—

$$\begin{array}{ccccccc} R\cdot N\cdot H & & R\cdot N\cdot H & & R\cdot N\cdot Br & & R\cdot N\cdot Br \\ | & \rightarrow & | & \rightarrow & | & \rightarrow & | \\ H\cdot N\cdot H & & H\cdot N\cdot Br & & H\cdot N\cdot Br & & Br\cdot N\cdot Br \end{array}.$$

The entire behaviour of the diazonium perbromides is in accord with this view of their constitution ; for example, they are in exactly the condition necessary for the typical diazo-decomposition to take place; this, in fact, occurs when they are heated, suspended either in chloroform or glacial acetic acid, thus :—

$$\begin{array}{ccccccc} R-N- & -Br & & R & & Br \\ | & & \rightarrow & | & + \equiv N + & | \\ Br-N- & -Br & & Br & & Br \end{array}.$$

All the members of the group of diazonium trihaloids have without doubt a similar constitution.

149. "*Cholestenone.*" By Charles Dorée and John Addymann Gardner.

Cholestenone, the ketone produced by the oxidation of cholesterol under suitable conditions, reacts with ozone in chloroform solution, giving an ozonide which most probably has the formula $C_{27}H_{44}O\cdot O_7$. This, when decomposed by water, gives carbon dioxide and a ketomonocarboxylic acid, $C_{26}H_{42}O_3$, which is identical with the one obtained by Windaus (*Ber.*, 1906, xxxix., 2008) by the oxidation of cholestenone with neutral permanganate. The work therefore confirms the opinion of Windaus that the double bond in cholestenone is situated in a terminal vinyl group. Cholesterol, on similar treatment, gives an ozonide, $C_{27}H_{46}O\cdot O_3$, which also evolves carbon dioxide on treatment with water.

Cholesterol therefore must possess a similar "carbon skeleton" to cholestenone, a point which had previously been regarded as doubtful.

150. "*Solubility of Silver Chloride in Mercuric Nitrate Solution.*" By Bertram Haward Buttle and John Theodore Hewitt.

The authors have studied the solubility of silver chloride in solutions of mercuric nitrate at 25°, using variable concentrations of mercuric nitrate, nitric acid, silver nitrate, and hydrochloric acid. Alteration in the concentration of the nitric acid, the other components remaining constant, has the effect of slightly increasing the precipitation of silver chloride.

From the results obtained when only the silver nitrate or hydrochloric acid is varied, the concentration of the other three components remaining unchanged, the authors arrive at the same conclusion as Morse (*Zeit. Phys. Chem.*, 1902, xli., 709), that when mercuric nitrate is present in large excess, chlorine only occurs as $HgCl\cdot$ ions.

151. "*The Relation between Absorption Spectra and Chemical Constitution.* Part IX. *The Nitroso- and Nitro-groups.*" By Edward Charles Cyril Baly and Cecil Henry Desch.

The absorption spectra of compounds containing the —NO and the $-NO_2$ groups have been examined. In order to guard against the disturbing influence of the benzene nucleus, the majority of compounds examined were aliphatic, several inorganic compounds being included for the sake of comparison. The results obtained show that both groups give rise to definite selective absorption, the oscillation frequency of which, in the case of the —NO group, is strikingly low. Moreover, it is found that the nature of the atom to which the above groups are directly linked exerts a very considerable influence on the position of the band.

(To be continued).

FARADAY SOCIETY.

Annual General Meeting, June 23rd, 1908.

Prof. A. K. Huntington, Vice-President, in the Chair.

The following Officers and Council were elected to serve for the ensuing year.

President—Sir Oliver Lodge, F.R.S.

Vice-Presidents—G. T. Beilby, F.R.S. ; R. A. Hadfield ; Geh. Reg.-Rat. Prof. W. Hittorf ; Prof. A. K. Huntington ; Lord Rayleigh, O.M., P.R.S. ; Prof. A. Schuster, F.R.S. ; Prof. J. J. Thomson, F.R.S.

Treasurer—F. Mollwo Perkin, Ph.D.

Council—Bertram Blount, F.I.C. ; A. C. Claudet, M.I.M.M. ; S. Z. de Ferranti, M.I.E.E. ; F. W. Harbord, F.I.C. ; R. S. Hutton, D.Sc. ; T. M. Lowry, D.Sc. ; H. F. K. Picard, M.I.M.M. ; James Swinburne, F.R.S. ; J. F. L. Vogel, M.I.E.E ; N. T. M. Wilsmore, D.Sc.

NOTICES OF BOOKS.

A Text-Book of Assaying. By C. and J. J. Beringer. Eleventh Edition. London : Charles Griffin and Company, Limited. 1908.

This work is one which has stood the test of time, and has been found to meet the needs both of students and of analytical chemists. It has been kept thoroughly well up-to-date, and only comparatively small changes have been made in the eleventh edition. The chapter on tin now includes the wet method, and the results obtained by vanning and wet assays are carefully compared and discussed. No better text-book on general assaying is to be procured, and students in schools of mines and assayers should not fail to get a copy.

Chemical Reagents. Their Purity and Tests. By E. Merck. Authorised Translation by Henry Schenck, A.B. (Harvard). London : Archibald Constable and Co., Ltd. 1907.

The issue of the report of the Committee on Purity of Reagents, appointed by the American Chemical Society in 1902, seems likely to be delayed for some years, since a considerable amount of work is still to be done, and a high standard of accuracy and precision is to be maintained. Hence the author of this book believes that in the meantime a revised translation of Merck's edition of Krauch's book "Die Prüfung der Chemischen Reagentien auf Reinheit" will be acceptable, and there is much truth in his contention that chemists will do wisely to make acceptance of their purchases conditional upon their coming up to the specifications of purity prescribed in this standard work. The text of the third edition of Krauch's book is closely followed, and the book contains the physical constants of all important and commonly used reagents, and full directions for testing them for purity. Some alterations and adaptations have been made for the benefit of English-speaking chemists, chiefly as regards the addition of acids of various strengths, *e.g.*, 99·5 per cent glacial acetic acid, which are to be obtained commercially in America but apparently not in Germany.

Laboratory Exercises in Physical Chemistry. By Frederick H. Getman, Ph.D. Second Edition. New York : John Wiley and Sons. London : Chapman and Hall, Limited. 1908.

An elementary course of practical work in physical chemistry is given in this book, and the theoretical aspects of the subject are also discussed fully enough to enable the student to dispense almost entirely with reference to larger and more complete works until he has become fairly well

acquainted with the practical methods and results of physical chemistry. A chapter on thermostats has been added to the second edition, and also some notes on radio-active measurements, while the chapter on chemical dynamics has been extended. A good deal of the practical work described is to be regarded rather as belonging to the domain of pure physics than physical chemistry, and in some respects the author has not made the ideal choice of material. For instance, no experiments on osmotic pressure are included, and methods of molecular weight determination are not collected together, but are scattered throughout the book. Moreover, it might have been wiser to omit the short chapter on spectroscopic work, or else to enlarge it very considerably; in its present form students would probably find that it needs much supplementing from other works.

Post's Chemisch-Technische Analyse. ("Post's Chemico-Technical Analysis"). Third Edition. Edited by Prof. Dr. Bernhard Neumann. Vol. I., Part IV. Braunschweig: Friedrich Vieweg and Sohn. 1908.

With this number the issue of the first volume of the third edition of Post's "Text-book of Analytical Chemistry" is completed. It contains chapters on the inorganic acids, including hydrofluoric acid, and on potash, saltpetre, and other salts of potassium, and it has been thoroughly revised and much increased in size and value. The chapter on bromine has been re-written by Dr. Bokemüller. The last chapter, which is also new, deals with antichlors, sodium sulphide, alumina, &c. The index to the whole of the first volume is included in this part, and it is hoped that the second volume, of which two parts have already appeared, will be finished very shortly.

Decoration of Metal, Wood, Glass, &c. By H. C. Standage. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1908.

This book contains a large collection of recipes for stains, dyes, &c., for use on metals, glass, wood, and porcelain. Methods of cleaning and renovating metals are described, and various miscellaneous processes, such as dyeing ivory, gilding book backs and edges, making imitation materials, etching, &c., are included. For painters and decorators and skilled workmen in the fancy trades the collection of formulæ will be of value, and the amateur may find in the book some suggestions which will save him the expense of employing outside assistance for small operations. It is certainly as useful as any book can be which deals with processes requiring in many cases considerable dexterity and long practice in order that they may be performed with anything approaching success.

Les Nouveautés Chimiques pour 1908. ("Chemical Novelties for 1908"). By Camille Poulenc. Paris: J. B. Baillière et Fils. 1908.

The arrangement of this work is identical with that adopted in previous years. In the first chapter physical apparatus which is used more particularly in chemistry is described, such as Blackman's apparatus for determining vapour densities, Quidor and Nachet's microscope, which is specially adapted for stereoscopic micrography, and Pulfrich and Löwe's spectrograph for photographing spectra. The second chapter deals with new chemical apparatus, and contains details relating to François' oven, Schlemmer's distilling column, Forestier's gas generator, and similar contrivances due to many other workers. Chapter III. is devoted to electrical apparatus used in chemistry, one of the most interesting being Gasparini's arrangement for electrolytic oxidation. New analytical apparatus, burettes, pipettes, calorimeters, &c., are included in Chapter IV., while in the last chapter are grouped together all classes of apparatus used in bacteriology.

CORRESPONDENCE.

THE POTENTIAL ENERGY OF THE ELEMENTS.

To the Editor of the Chemical News.

Sir,—In reply to Mr. H. Stanley Redgrove in the Chemical News of July 3rd (vol. xcviii., p. 11) *re* my paper on "The Potential Energy of the Elements," I may mention that the values were obtained by me in the course of an investigation into the fundamental characters and correlation of the elements, on which I am still engaged. To explain the method of obtaining these values would necessitate entering into a much larger question which would require more space than I could expect you to afford me.—I am, &c.,

Daniel J. Rankin.

July 4, 1908.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. cxlvi., No. 23, June 9, 1908.

Direct Hydrogenation of Polyphenols. — Paul Sabatier and A. Mailhe.—The general method of direct hydrogenation by contact with divided nickel can be applied to the transformation of benzene and its homologues into cyclohexane and its homologues. It can also be used to convert phenols into the corresponding cyclohexanols, aniline and its substituted derivatives into cyclohexylamine and its homologues. The method as originally described cannot, however, be applied to di- and triphenols, which under the action of nickel above 200° yield benzene, phenol, cyclohexanol, and cyclohexane. By lowering the temperature of hydrogenation considerably it is possible to fix six atoms of hydrogen on to hydroquinone. pyrocatechin, and pyrogallol. The temperature is kept at 130°, and a very rapid current of hydrogen is passed over the polyphenol in presence of reduced nickel.

Catalytic Dehydration of Organic Compounds.—J. B. Senderens.—Precipitated alumina rendered anhydrous by drying below a red heat is an excellent catalysing agent, excelling silica, magnesium phosphates, &c., in this respect. (When too strongly heated alumina is a bad catalyser). Ethyl oxide yields ethylene, and from acetic acid acetone can readily be obtained. Precipitated alumina is also capable of removing one molecule of hydracid; thus isobutylchloride at 250° yields hydrochloric acid and isobutylene.

Action of Silver Nitrate on Chloroauric Acid and Preparation of Fulminating Gold.—Jules Jacobsen.—When silver nitrate is added to a solution of chloroauric acid a precipitate containing all the gold and all the chlorine is obtained:—

$$AuCl_3HCl + 4AgNO_3 + 3H_2O = Au(OH)_3.4AgCl + 4HNO_3.$$

This precipitate gives with ammonia a gelatinous precipitate of fulminating gold, the silver chloride being dissolved out. The product possesses high explosive power. It is more stable when wet than when dry. The formula is $Au(OH)_2NH_2$ or $(AuN.2H_2O)$.

Separation of Ammonia and Amines by means of Boiling Absolute Alcohol.—Jean Bertheaume.—The author has studied the solubility in absolute alcohol of monomethylamine chloride, ammonium chloride, and a mixture of these two substances, and has found that when a mixture is treated with boiling absolute alcohol, filtered, and the filtrate evaporated, a minimum of 8·5 per cent of ammonium chloride is retained by the amine.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xli., No. 9, 1908.

Simple Test for Glycuronic Acid by means of Naphthoresorcin, Hydrochloric Acid, and Ether.—B. Tollens.—With hydrochloric acid and phloroglucin arabinose, xylose, and glycuronic acid all give colour and spectral reactions, but when heated with hydrochloric acid and naphthoresorcin the two pentoses give a strong fluorescence but no characteristic colour or spectral reactions, while glycuronic acid differs from them in giving a blue coloration and a spectral band on the D line. The blue substance is soluble in ether, to which it imparts a blue or blue-violet colour, and its formation, together with the appearance of the dark spectral band lying near the D line, can be employed as a sensitive test for glycuronic acid.

Detection of Nickel and Cobalt when present together.—Hermann Grossman and Walter Heilborn.—Ammonia is added to the fairly concentrated solution containing the two metals, and then a 10 per cent solution of cane-sugar and dicyandiamidin-sulphate solution (Grossmann's "nickel reagent"). Finally caustic soda is added. When much nickel is present a yellow or reddish-yellow coloration is produced, while the presence of large quantities of cobalt causes the solution to turn red or reddish-violet. Thus fractions of a milligrm. of cobalt in presence of more than 100 times the quantity of nickel can be detected by the violet coloration, while if much cobalt and only a little nickel is present, crystalline nickel dicyandiamidin is always precipitated. This test is very accurate and rapid.

Picrates.—W. Suida.—Picric acid and anthranilic acid form two compounds containing one molecule of picric acid to one molecule of anthranilic acid, and one molecule of picric acid to two molecules of anthranilic acid respectively. This behaviour of anthranilic acid is not due to its amphoteric character, for similar well characterised compounds of toluidine with picric acid are formed. Both compounds in which the molecular proportions are 1 : 1 are faintly coloured, while those containing one molecule of picric acid to two molecules of base are strongly coloured, both when hydrated and in the anhydrous state.

Solutions of Alkali Metals in Liquid Ammonia.—Otto Ruff and Julian Zedner.—The authors have confirmed their conclusions that the substances described by Joannis as metallic ammonium compounds are really the pure metals with a deposit of supersaturated solution in liquid ammonia upon them. For this purpose they have plotted the boiling and melting-point curves of ammonia solutions of potassium, sodium, and lithium of very different concentrations. From the melting-point diagram, especially with sodium, it is seen that within a certain interval of temperature two liquid phases exist between fairly wide concentration limits. It seems not improbable that a compound of formula $Na.5NH_3$ exists.

Hydrogen Persulphide.—Ignaz Bloch and Fritz Höhn.—Hydrogen persulphides corresponding to the formulæ H_2S_2, H_2S_3, H_2S_5, H_2S_6, H_2S_7, and H_2S_8 have been prepared, though in no case in a pure state. The best characterised of these are the derivatives of the compounds H_2S_6 and H_2S_8, which have been obtained and analysed by different investigators. By the action of dilute hydrochloric acid upon sodium polysulphide at a temperature from $-10°$ to about $0°$, an oil consisting of raw hydrogen persulphide can be obtained. From the analysis of the purified product it is clear that Rebs' statement, that whatever polysulphide is used the compound formed is always H_2S_5, is incorrect. Unless special precautions are taken no single chemical compound is obtained.

Hydrotrisulphide.—Ignaz Bloch and Fritz Höhn.—Raw hydrogen persulphide prepared from sodium polysulphide when subjected to fractional distillation in an apparatus through which a current of dry hydrochloric acid gas has been led (to neutralise the alkalinity of the glass) yields a distillate which has the composition H_2S_3. Hydrotrisulphide is a colourless liquid with a sharp smell, recalling carbon disulphide and camphor. When warmed it yields H_2S. It is inflammable and is decomposed by alkalis. Concentrated sulphuric acid reacts slowly with it, giving sulphur dioxide. It behaves like a reducing and sulphating agent, and is also capable of acting as an oxidiser.

Hydrodisulphide.—Ignaz Bloch and Fritz Höhn.—When the receiver in which the hydrotrisulphide described in the preceding article is cooled, it is found that the percentage of H_2S in the product is high; this is due to the presence of some disulphide, H_2S_2. When the receiver is gently heated and the product is received in another cooled vessel, a yellowish, clear, liquid consisting of pure H_2S_2 is obtained. It is inflammable, and is decomposed by distilled water and by alkalis. Concentrated sulphuric acid also decomposes it, yielding amorphous sulphur and sulphur dioxide.

Constitution of Hydrodisulphide and Hydrotrisulphide.—Ignaz Bloch.—The compounds of hydrogen and sulphur appear to be formed by successive substitutions of HS for H in the lowest member of the series H_2S. Thus $HS.H \rightarrow HS.HS$ or H_2S_2; $HS.HS \rightarrow HS.S.HS$ or H_2S_3. Undoubtedly higher members of this series exist. Corresponding polysulphides are known, *e.g.*, $(NH_4)_2S$, $(NH_4)_2S_2$, $(NH_4)_2S_3$, $(NH_4)_2S_4$, $(NH_4)_2S_5$, $(NH_4)_2S_7$, $(NH_4)_2S_8$, $(NH_4)_2S_9$.

MISCELLANEOUS.

The Seventh International Congress of Applied Chemistry will be held in London, from May 27th to June 2nd, 1909. An Organising Committee has been formed for the purpose of making all arrangements for the holding of the Congress in London. This Committee consists of representatives of the following Societies:—Royal Societies of London, Edinburgh, and Dublin, Society of Chemical Industry, Chemical Society, Institute of Chemistry, Society of Public Analysts, Royal Society of Arts, Iron and Steel Institute, Institution of Mining Engineers, Institution of Mining and Metallurgy, Society of Dyers and Colourists, International Association of Leather Chemists, Institute of Brewing, Royal Agricultural Society of England, The Lawes Agricultural Trust, Pharmaceutical Society, Royal Photographic Society, Faraday Society, London Chamber of Commerce (Chemical Trade Section), representing all the most important industries. Previous Congresses have been held in Brussels (1894), Paris (1896), Vienna (1898), Paris (1900), Berlin (1903), and Rome (1906). The work of the Congress has steadily grown in importance, and it is hoped that the London Congress may be a worthy successor to those which have gone before. The scope of the work of the Congress is indicated by the following list of Sections and Presidents:—Analytical Chemistry—Dr. T. E. Thorpe, C.B., F.R.S. Inorganic Chemistry and Allied Industries—Dr. Ludwig Mond, F.R.S. Metallurgy and Mining—Sir Hugh Bell, Bart. Explosives—Sir Andrew Noble, Bart., K.C.B., F.R.S. Organic Products—Prof. W. H. Perkin, F.R.S. Colouring Substances and their Uses—Prof. Meldola, F.R.S. Industry and Chemistry of Sugar—Richard Garton, Esq. Starch Industry—Dr. Horace T. Brown, F.R.S. Fermentation—John Gretton, Esq., M.P. Agricultural Chemistry—Lord Blyth. Hygiene and Medical Chemistry—Sir J. Crichton-Browne, F.R.S. Pharmaceutical Chemistry—N. H. Martin, Esq. Bromatology—Robert R. Tatlock, Esq., F.I.C. Photographic Chemistry—Sir W. de W. Abney, K.C.B., F.R.S. Electrical and Physical Chemistry—Sir John Brunner, M.P. Law, Political Economics, and Legislation with reference to Chemical Industries—Lord Alverstone. Committees are being formed in the different countries for the purpose of furthering the interests of the Congress. At a later date, further particulars will be sent out; meantime, the undersigned will be happy to give any explanations that may be desired—Wm. Macnab, Honorary Secretary, 10, Cromwell Crescent, S.W.

THE CHEMICAL NEWS.

VOL. XCVIII., No. 2538.

ON THERMO-CHEMICAL EVIDENCE FOR VON BAEYER'S STRAIN THEORY.

By H. STANLEY REDGROVE, B.Sc. (Lond.), F.C.S.

Introduction.

IT has already been pointed out that the thermal behaviour of the hydrocarbons whose molecular heats of combustion have been determined by Thomsen are in agreement with Baeyer's strain theory (see CHEMICAL NEWS, xcv., 301). The argument is repeated here at greater length in order that the following new calculations may be perfectly intelligible.

Considering, firstly, the "ethene" and "ethine" links. If an ethene link were a double link in an arithmetical sense we should have $L_2 - 2L_1 = 0$, whereas actually $L_2 - 2L_1 = 2(2H - L_1) - (4H - L_2) = 2\beta - \gamma = 16{\cdot}0$ cals. Similarly, $L_3 - 3L_1 = 3(2H - L_1) - (6H - L_3) = 3\beta - \delta = 44{\cdot}5$ cals. We know, however, from pure chemistry that a "double" link is not an arithmetical double link, and that a "treble" link is not an arithmetical treble link, but in so far as stability is concerned each is less than a "single" link.

The instability of ethane and ethine links finds a mathematical interpretation in von Baeyer's strain theory, which states that the four valencies of the carbon atom normally act in the directions of the four lines drawn from the centre to the four corners of a regular tetrahedron (*i.e.*, making an angle of 109° 28′ with one another). If the directions of the valencies are different from this normal condition a state of intramolecular strain is set up, the magnitude of the strain depending upon the angle through which the valencies are diverted.

The tendency of the strain is to sever the link, hence the instability of such links; moreover, the molecular heat of combustion of a compound, which is in a condition of intramolecular strain, will be greater than the calculated by the thermal equivalent of this strain. Hence, if we express this thermal equivalent for the "double" link by T_2, and for the "treble" link by T_3, then $2L_1 + T_2 = L_2$, whence $T_2 = 16{\cdot}0$ cals., and $3L_1 + T_3 = L_3$, whence $T_3 = 44{\cdot}5$ cals.

In the polymethylenes, although there are no "double" or "treble" links, we can readily see by constructing models of the molecules that they are in a condition of strain. Assuming that they possess a regular configuration and that the atoms constituting the ring are all in one plane, we obtain for the angle of deviation the values shown in Table I., the general formula being:—

$$D^\circ = 54^\circ\,44' - \frac{n-2}{n}\,90^\circ,$$

where n is the number of carbon atoms in the ring and D° the angle of deviation.

TABLE I.

Ring.	D°.
Dimethylene (=ethylene)	54° 44′
Trimethylene	24° 44′
Tetramethylene	9° 44′
Pentamethylene	0° 44′
Hexamethylene	−5° 16′
also—	
Acetylene	70° 32′

This explains to a great extent the relative stabilities of the various groups of polymethylenes.

The molecular heat of combustion of trimethylene determined by Thomsen (*i.e.*, 498·0 cals.) was found to be considerably greater than the calculated (*i.e.*, 474·9 cals.). This excess (which we will represent by $T_{III.}$) is consequently the thermal equivalent of the intramolecular strain in this compound, so that $T_{III.} = (498{\cdot}0 - 474{\cdot}9)$ cals. $= 23{\cdot}1$ cals.

Thomsen's determinations (save that of the molecular heat of combustion of ethylene oxide) do not afford further data for testing the accuracy of von Baeyer's strain theory. However, Stohmann has carried out a research on the heats of combustion of polymethylene compounds. The

TABLE II.

		M.H.C. constant volume (Stohmann). Cals.	Mean. Cals.
1. Dimethylenes (ethylenes)*—			
Fumaric acid	$C_4H_4O_4$	320·7	320·7
Succinic acid	$C_4H_6O_4$	357·1	357·1
Therefore $\beta - T_2 = 36{\cdot}4$ cals.			
Dimethyl fumarate	$C_6H_8O_4$	664·7	664·7
Dimethyl succinate	$C_6H_{10}O_4$	703·3	703·3
Therefore $\beta - T_2 = 38{\cdot}6$ cals.			
Mean $\beta - T_2 = 37{\cdot}5$ cals.			
2. Trimethylenes—			
$\alpha\alpha$-Trimethylenedicarboxylic acid	$C_5H_6O_4$	483·5	483·95
$\alpha\beta$-Trimethylenedicarboxylic acid	$C_5H_6O_4$	484·4	
Glutaric acid	$C_5H_8O_4$	515·0	515·85
Methyl succinic acid	$C_5H_8O_4$	515·2	
Ethyl malonic acid	$C_5H_8O_4$	517·9	
Dimethyl malonic acid	$C_5H_8O_4$	515·3	
Therefore $\beta - T_{III.} = 31{\cdot}9$ cals.			
$\alpha\alpha\beta\beta$-Tetramethyl trimethylenetetracarboxylate	$C_{11}H_{14}O_8$	1170·7	1170·7
Tetramethyl methylenedimalonate	$C_{11}H_{16}O_8$	1202·2	1202·2
Therefore $\beta - T_{III.} = 31{\cdot}5$ cals.			
Mean $\beta - T_{III.} = 31{\cdot}7$ cals.			
3. Tetramethylenes—			
$\alpha\alpha$-Tetramethylenedicarboxylic acid	$C_6H_8O_4$	642·4	642·45
$\alpha\beta$-Tetramethylenedicarboxylic acid	$C_6H_8O_4$	642·5	
Adipic acid	$C_6H_{10}O_4$	668·6	671·84
Methylglutaric acid	$C_6H_{10}O_4$	670·5	
Ethyl succinic acid	$C_6H_{10}O_4$	671·9	
Sym. dimethyl succinic acid	$C_6H_{10}O_4$	670·7	
Unsym. dimethyl succinic acid	$C_6H_{10}O_4$	671·4	
Propyl malonic acid	$C_6H_{10}O_4$	674·7	
*iso*Propyl malonic acid	$C_6H_{10}O_4$	674·9	
Methyl ethyl malonic acid	$C_6H_{10}O_4$	672·0	
Therefore $\beta - T_{IV.} = 29{\cdot}4$ cals.			
4. Pentamethylenes—			
$\alpha\beta$-Pentamethylenedicarboxylic acid	$C_7H_{10}O_4$	775·7	775·7
Pimelic acid	$C_7H_{12}O_4$	828·3	828·3
Therefore $\beta - T_{V.} = 52{\cdot}6$ cals.			
5. Hexamethylenes—			
cis-Hexahydroterephthalic acid	$C_8H_{12}O_4$	928·0	928·45
trans-Hexahydroterephthalic acid	$C_8H_{12}O_4$	928·9	
Suberic acid	$C_8H_{14}O_4$	982·8	982·8
Therefore $\beta - T_{VI.} = 54{\cdot}35$			

* Maleïc acid is omitted as it gives a divergent result.

first part of this paper deals with the interpretation of Stohmann's experimental results, the second with ethylene oxide.

1. *Interpretation of Stohmann's Experimental Results for the Molecular Heats of Combustion of Polymethylene Compounds.**

The procedure adopted by Stohmann and his collaborators was to determine the heat of combustion of polymethylene carboxylic acids and the corresponding open-chain acids.

The difference between the molecular heats of combustion of any polymethylene compound and the corresponding open-chain compound, is due to the breaking of the ring and the addition of two hydrogen atoms linked to carbon; in terms of our constants this difference equals $2H - L_I - T$; *i.e.*, $\beta - T$.

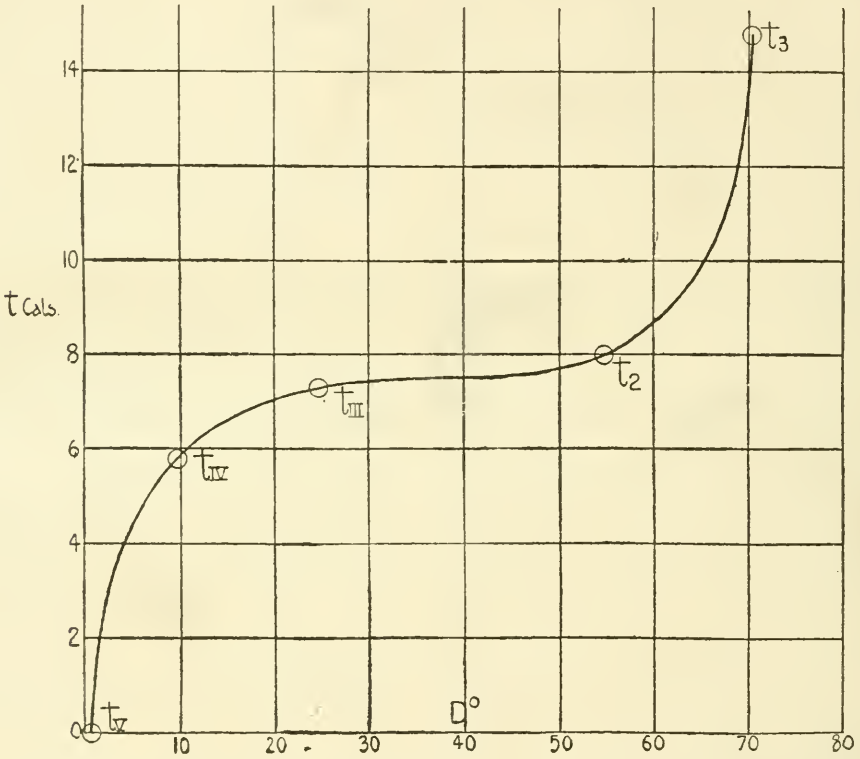
only 1·0 cal. in the case of T_2 and 2·3 cals. in the case of T_{III}.

TABLE III.

Ring.	Stohmann. Cals	Cals.	Thomsen. Cals.
Acetylene . .	—		$T_3 = 44·5$
Ethylene	$T_2 = 52·5 - 37·5$	= 15·0	$T_2 = 16·0$
Trimethylene . .	$T_{III.} = 52·5 - 31·7$	= 20·8	$T_{III.} = 23·1$
Tetramethylene	$T_{IV.} = 52·5 - 29·4$	= 23·1	
Pentamethylene	$T_{V.} = 52·5 - 52·6$	= −0·1*	
Hexamethylene	$T_{VI.} = 52·5 - 54·35$	= −1·85*	

* Zero.

Now, as in the above rings varying numbers of links are concerned, it is evident that, in order to obtain comparable results, it will be necessary to divide the thermal equivalent



In Table II. are given these molecular heats of combustion (for constant volume), and the values of $\beta - T$ calculated for each ring. The notation employed is to denote the number of carbon atoms in the ring by a Roman numeral affixed to T.

The value of β being known, the values of T can be at once obtained, as in Table 3. Perfectly accurate results cannot be expected, for the value of β (= 52·5 cals.) is calculated from the molecular heats of combustion of gases, whereas the values of $\beta - T$ are for solids. However, as $\beta - T$ is always found as the *difference* between two of Stohmann's experimental results, the error introduced will be at a minimum, and fairly good approximate results may be hoped for.

On comparing with the above those values of T which have also been found entirely from Thomsen's experiments (namely, T_2 and $T_{III.}$) we see the difference amounts to

of the total strain in each ring (T) by the number of links in that ring which are in a condition of strain, thereby obtaining the thermal equivalents of the strain set up by deviating one C.C link through various angles, represented by t in Table 4.

TABLE IV.

Thermal equivalent of strain for one link.

Ring.		Stohmann. Cals.	Thomsen. Cals.	Mean. Cals.	Angle of deviation. D°.
Acetylene . .	t_3 =	—	14·8	—	70° 32′
Ethylene	t_2 =	7·5	8·0	7·75	54° 44′
Trimethylene . .	$t_{III.}$ =	6·9	7·7	7·3	24° 44′
Tetramethylene	$t_{IV.}$ =	5·8			9° 44′
Pentamethylene	$t_{V.}$ =	0·0			0° 44′

It appears from this table that the value of t depends upon that of D° (although the relation is evidently not that of a simple proportion), for as D° increases, t increases. This regularity is best exhibited by a curve obtained by

* See Stohmann, Kleber, and Langbein, *Journ. Prakt. Chem*, xl., 202; Stohmann and Kleber, *Ibid.*, xliii., 1, and xlv., 475.

plotting D° and t along co-ordinate axes (the values used being Thomsen's for t_3 and t_2; Stohmann's for $t_{IV.}$ and $t_{V.}$; and the mean of Thomsen's and Stohmann's for $t_{III.}$). Its regular nature is at once apparent, but up to the present the author has not been able to satisfactorily represent the relation between D° and t by any simple formula.

2. *Interpretation of Thomsen's Experimental Result for the Molecular Heat of Combustion of Ethylene Oxide.*

Chemical evidence shows that ethylene oxide has the constitution $O\begin{matrix}CH_2\\|\\CH_2\end{matrix}$, so that its molecular heat of combustion is represented by $2\alpha-\beta-\omega$.* The molecular heat of combustion (corrected for constant volume) of this compound, was found by Thomsen to be 311·7 cals., whereas the calculated amounts to only $(2\times210\cdot8-52\cdot5-75\cdot4)$ cals. = 293·7 cals., so that the experimental is considerably greater (by 18·0 cals.) than the calculated molecular heat of combustion. The molecular heat of formation deduced from the experimental molecular heat of combustion, namely, 17·2 cals., is correspondingly less than the calculated, namely, $2\alpha'-\beta'-\omega' = (2\times21\cdot2-15\cdot0+7\cdot8)$ cals. = 35·2 cals.

This apparently anomalous result would, however, be expected from the standpoint of von Baeyer's strain theory, for from analogy with trimethylene the ethylene oxide molecule must be in a state of strain. The thermal equivalent of this strain is now given as 18·0 cals.; that it is not identical with that for trimethylene is only to be expected from the fact that carbon has an affinity for carbon differing from that which it has for oxygen, and, moreover, it is not improbable that the normal directions of the oxygen valencies are different from the normal directions of carbon valencies.

The conclusion to be drawn from the thermal data considered, is that it is in perfect accord with von Baeyer's strain theory, thereby supplying satisfactory evidence of the general validity of this theory.

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EXPLOSIVE CRYSTALLISATION.

By FRANK E. WESTON, B.Sc.

In the course of an investigation that is being carried out in this laboratory it was found necessary to attempt the crystallisation of a solution in a partial vacuum. The solution was an aqueous one of a compound formed by the combination of a sulphate with a thiosulphate. The solution, contained in a 6 in. evaporating basin, was placed on a porcelain dish partially filled with concentrated sulphuric acid, the latter dish standing on a ground glass plate, ¼ in. thick by 12 in. square; the whole was covered with a bell-jar, 7 in. diameter and 8 in. high, fitted with a cork carrying a glass tap, and made perfectly air-tight by sealing the surface of contact of bell-jar and plate with paraffin wax. The solution was allowed to evaporate for three weeks at a pressure of about half an atmosphere, during which time it evaporated very slowly. At the end of this period the pressure was reduced by means of a water-pump to about 20 mm., and was so left on Wednesday evening, July 1st, at 9.30 p.m. On Thursday morning, July 2nd, at 10 a.m., on going to examine the solution, it was found that the basin was broken into several pieces, the solution was splashed all over the bell-jar, the glass plate cracked into a dozen pieces, and a large star-shaped crack was found in the shoulder of the bell-jar; the bell-jar was still firmly fixed to the glass plate and the solution had partially percolated through the cracked plate into the wooden base; on opening the tap and carefully removing the jar it was found to be full of SO_2, evolved by the action of H_2SO_4 on the thiosulphate. The apparatus had been touched by no one, and consequently no reason could be assigned for what had happened. On Friday, July 3rd, an attempt was made to crystallise two solutions of a sulphite *in vacuo*. The solutions were saturated (and probably supersaturated) and were placed in a similar apparatus excepting that fused $CaCl_2$ took the place of the H_2SO_4, and the second basin rested on a tripod stand that stood on the glass plate. The pump was set working and in half-an-hour the pressure had fallen to about 20 mm.; suddenly the top basin was seen to bump violently, and its contents partly ejected with a dull thud, and before the apparatus could be touched the basin had broken into half-a-dozen pieces, which on falling disturbed the bottom basin and upset its contents; at the same time the whole apparatus seemed to be shaken, with the result that the glass plate was cracked into several pieces and air violently entered the jar.

The bell-jar still remained firmly fixed to the plate, and on removing it no trace of SO_2 was evident, nor had any apparent decomposition taken place. Some of the pieces of the broken basin had a fine crystalline deposit on them.

It seems probable that crystallisation was suddenly induced on the surface of the basin, with a consequent sudden increase in the vapour pressure of the surrounding liquid, which, under the very low pressure existing in the bell-jar, caused the liquid to boil violently, the reacting force causing the basin to bump violently and hence to break; the phenomenon was accompanied with a slight but distinct explosive noise.

Further experiments are being carried out with a view to confirming the theory put forward, and other solutions which are known to be supersaturated are also being examined.

The Chemical Laboratory,
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July 4th, 1908.

* For the meaning of ω see CHEMICAL NEWS, xcvii., p. 253.

THE HOMOGENEITY OF TELLURIUM.

By VICTOR LENHER.

When tellurium or its dioxide reacts with a number of the liquid anhydrous chlorides, crystals of tellurium tetrachloride or of a double chloride are formed along with a mother-liquor which contains the excess of the reacting anhydrous chloride (see CHEMICAL NEWS, xcviii., p. 4). This mother-liquor contains such by-products of the reaction as may be soluble in it, and has also been found invariably to contain greater or less quantities of tellurium.

When sulphur monochloride is the reacting liquid, the amount of tellurium appearing in the excess of the reagent is quite small, so small indeed that a fairly good separation of tellurium from selenium can be effected by use of this reagent in the cold, inasmuch as selenium dissolves readily in sulphur monochloride. When, however, the sulphur chloride is warm, its solvent power on tellurium chloride is materially increased.

Other chlorides studied, such as thionyl chloride, sulphuryl chloride, phosphorus oxychloride, and antimony pentachloride, when in excess, dissolve considerable quantities of tellurium chloride or of the double chloride as the case may be.

Inasmuch as the question of the complexity of tellurium has been repeatedly raised, especially so after the prediction of Mendeleeff in his London address (*Journ. Chem. Soc.*, lv., 649), when he predicted that tellurium contained another element, whose atomic weight would be 212, and which he called dvi-tellurium; and after the work of Brauner (*Ibid.*, lv., 411), when he thought from some of his experiments that the so-called element was actually a composite, it has been deemed important to examine these mother-liquors, arising from the reactions above indicated, to ascertain whether any of the reagents studied would possibly allow of a splitting apart of tellurium.

Norris, Fay, and Edgerley (*Am. Chem. Journ.*, xxiii., 105) studied the elementary character of tellurium by carrying out an elaborate fractional crystallisation of the double bromide of tellurium and potassium. Later Norris (*Journ. Am. Chem. Soc.*, xxviii., 1675) made fractional distillations of tellurium oxide, following the distillations by determinations of the atomic weight. The conclusions drawn by Norris are that his results have furnished positive evidence in favour of the elementary character of tellurium.

Baker and Bennet have recently published an account of their investigations on the atomic weight and elementary character of tellurium (*Journ. Chem. Soc.*, xci., 1849). Their work was carried on for a period of thirteen years. They studied the fractional crystallisation of telluric acid, the progressive solubility of barium tellurate, the fractional distillation of the metal, chloride and dioxide, the fractional decomposition of the hydride; the fractional electrolysis of the bromide and chloride, and the fractional precipitation of the chloride by water. They have been unable to distinguish any difference in the atomic weight, and consider 127·6 to be the true atomic weight.

Study of the Products of the Reaction of various Anhydrous Chlorides on Tellurium and its Oxide.—The mother-liquor arising from each of the reactions studied was decomposed by water, and the tellurium precipitated from hydrochloric acid solution by sulphur dioxide, after which it was carefully purified from such materials as might be introduced by the reagents used.

In each case the tellurium obtained was found to answer to all of the tests to which the original material responded, and behaved in all respects similarly to what we commonly know to be tellurium.

The method of approaching this problem can be illustrated by the experiments in which the action of phosphorus oxychloride on tellurium dioxide was studied. In this case a crystalline compound is found which careful analysis has shown to have the composition $TeCl_4.POCl_3$. The excess of phosphorus oxychloride used was observed to carry considerable quantities of tellurium in solution. This mother-liquor was carefully decanted from the crystallised salt and treated with water. By this procedure, the phosphorus oxychloride is converted into phosphoric and hydrochloric acids and the tellurium tetrachloride decomposed into hydrated dioxide.

After addition of sufficient hydrochloric acid to completely dissolve the tellurium dioxide, treatment with sulphur dioxide yielded elementary tellurium. It has been observed in working with this particular liquid that when an attempt is made to precipitate tellurium out of a solution containing a large quantity of phosphoric acid, the reaction is very much retarded and the tellurium precipitates very slowly. This can be overcome, in a large measure, by the addition of hydrochloric acid and considerable dilution with water. The retardation of precipitation of tellurium in presence of phosphoric acid is doubtless due to lack of dissociation, and the precipitation can better be effected after addition of considerable quantities of hydrochloric acid.

The tellurium, after having been converted into chloride by means of aqua regia, was again precipitated by sulphur dioxide, converted into the basic nitrate, and crystallised from nitric acid solution, as has been suggested by Norris, Fay, and Edgerley for the purification of tellurium (*Am. Chem. Soc.*, xxiii., 105). The basic nitrate, when ignited, gave the dioxide.

Determination of the amount of tellurium in the dioxide by precipitation as element gave the ratio—

TeO_2	0·85635
Te	0·6845
Atomic weight Te..	127·52

The tellurium thus obtained from the excess of phosphorus oxychloride showed by the ratio of tellurium dioxide to element that no apparent change in atomic weight had aken place, and that no splitting apart of the element had occurred was evidenced by the fact that the salt $TeCl_4.POCl_3$ which did not dissolve in the excess of phosphorus oxychloride, and which contained all of the tellurium not appearing in the mother-liquor, showed by analysis a rational formula with tellurium taken at the commonly accepted atomic weight.

The mother-liquors appearing in all the reactions of the anhydrous chlorides which were brought in contact with tellurium or the dioxide were examined in a manner similar to that with phosphorus oxychloride, and the same character of results were obtained. A rational formula for the insoluble crystalline product always appeared when a careful analysis was made, while the tellurium appearing in the mother-liquor, after decomposing the excess of reagent and purifying the element from such products of the reaction as might contaminate it, always showed the ratio of tellurium dioxide to element corresponding to the atomic weight of 127·5 for tellurium.

Tellurium and Ferric Chloride.—By heating together in the dry condition tellurium and anhydrous ferric chloride, reaction ensues with the production of ferrous chloride and tellurium tetrachloride. This reaction can also be accomplished and much more conveniently so by the continued action of a hot solution of ferric chloride on tellurium, $4FeCl_3 + Te = TeCl_4 + 4FeCl_2$. Pethybridge (U.S. Patent No. 709,037, Sept. 16, 1902) has studied the action of a solution of ferric chloride having a density of 1·18 on telluride gold ores, and claims to be able to extract the tellurium as tetrachloride with the simultaneous formation of ferrous chloride, leaving behind gold and silver as follows:— $8FeCl_3 + (AuAg)Te_2 = 2TeCl_4 + 8FeCl_2 + (AuAg)$.

This is in line with the results previously obtained by the author (*Journ. Am. Chem. Soc.*, xxiv., 355), which indicate that the tellurium in the natural tellurides of gold is not strongly united to the gold.

While tellurium reduces ferric chloride to ferrous with the simultaneous production of the tetrachloride, ferrous salts will precipitate a part of the tellurium when added in excess to a solution of the tetrachloride in hydrochloric acid.

Crane (*Am. Chem. Journ.*, xxiii., 408) and Rose (*Pogg. Ann.*, xxi., 443) have attributed this precipitation of small quantities of tellurium by means of ferrous sulphate to the presence of tellurium dichloride in the tetrachloride. Tellurium dichloride is, however, decomposed by water or aqueous hydrochloric acid into the element and oxide or chloride, and with the knowledge that tellurium dissolves in hydrochloric acid in the presence of the air to tetrachloride directly, it would seem that the precipitation of small quantities of tellurium by means of ferrous salts is largely controlled by mass action. The reactions between ferric chloride and tellurium and ferrous salts and hydrochloric acid solutions of the tetrachloride are indeed reversible.

In view of this partial precipitation of tellurium by ferrous salts, a series of experiments was conducted, in which this partial precipitation was made the basis of a fractionation. To this end a quantity of tellurium originally obtained from the Baltimore Smelting and Rolling Co. was precipitated from a caustic soda solution by means of grape-sugar. The carefully washed material was dissolved in aqua regia and was precipitated by sulphur dioxide from a hydrochloric acid solution. The tellurium thus obtained was fused with pure potassium cyanide, the resulting fusion extracted with water, and a current of air passed through the solution to precipitate the tellurium out of the solution of the alkaline telluride, leaving sulphur or selenium present in solution as alkaline thiocyanate or selenocyanate. The tellurium purified in this manner was introduced into a porcelain boat which was placed in a porcelain tube. This tube was connected with a supply of hydrogen, which was generated from pure zinc and hydrochloric acid and which was washed with water. The tellurium was distilled from the boat (the tube being heated by a blast lamp) into the cooler portion of the tube where it was condensed. The distilled metal was collected and

introduced again into a clean porcelain boat and tube and the distillation repeated.

Twenty-five grms. of this metal were dissolved in a mixture of nitric and hydrochloric acids and a hydrochloric acid solution of the tetrachloride formed by boiling off the excess of nitric acid. To this solution was added a solution containing about 25 grms. of ferrous sulphate, which contained a small amount of ferric salt, when a precipitate of about 0·1 grm. of elementary tellurium appeared. The quantity of precipitate obtained did not appear to be materially increased by the addition of a considerably larger quantity of the ferrous sulphate solution. The solution containing the tellurium and iron salts was treated with acid sodium sulphite and the tellurium precipitated. This tellurium was then re-converted into chloride by means of hydrochloric and nitric acids, and ferrous sulphate again added to the hydrochloric acid solution. A second precipitate of about the same size as before appeared. This operation was repeated twenty-four times, fractions being obtained each time of approximately the same size. These twenty-four precipitates were combined, dissolved in hydrochloric and nitric acids, and a hydrochloric acid solution obtained as before. Treatment of this solution with ferrous sulphate again yielded a small precipitate of tellurium, the size of the precipitate being about the same as in the previous series of fractions. A second precipitation was made and was combined with the previous one for an atomic weight determination. The metal was treated with nitric acid in a small Jena flask, and the resulting basic nitrate gradually heated to 440°, when the weight was found to be constant. 0·1694 Te gave 0·2119 TeO_2, and if O = 16, Te = 127·55.

Inasmuch as the original material showed the same atomic weight, it is evident that by this method of fractionation no portion can be found which shows a figure radically different from the commonly accepted figure.

Action of Hydrochloric Acid on Tellurium in presence of Air.—Although tellurium is ordinarily considered as insoluble in hydrochloric acid, yet it is actually attacked slightly by the acid when exposed to the air, if sufficient time is allowed for contact. This action can be demonstrated by bubbling a current of air, for several weeks, through concentrated hydrochloric acid in which is suspended metallic tellurium. In a comparatively short time the acid becomes yellow, indicating the presence of tetrachloride.

This action of hydrochloric acid on tellurium in the presence of air has been made the basis of an experiment in which it would be possible to have differential solution take place should tellurium contain a higher member of the series of elements in which it is commonly placed.

One hundred grms. of carefully purified tellurium was precipitated from hydrochloric acid solution by means of sulphur dioxide, and the precipitate washed until the wash-water would not react for chloride with silver nitrate. This freshly precipitated and finely divided metal was introduced with pure concentrated hydrochloric acid into a filtering flask, and a current of air which had been previously washed with water and then passed through pure hydrochloric acid was drawn through the solution for three months. At the end of this time a considerable part of the metal had dissolved. The solution was filtered, and on treatment of the solution with acid sodium sulphite, tellurium was precipitated. Two portions of tellurium were here obtained, one of which was a smaller portion of a few grms. obtained from a tellurium solution that had been formed by the slow action of hydrochloric acid and air on tellurium, and this solution had remained in contact with the main part of the finely divided metal for three months. The portion which dissolved and that still remaining undissolved were found to be identical in chemical character, obeyed the same reactions, and when converted into oxide, and this oxide analysed, gave an atomic weight of 127·5.

In the hands of the author, tellurium has shown no signs of breaking apart in any of the reactions which had for their object a study of the elementary character of the metal, nor in the various reactions or derivatives which have been studied in our laboratory has the element shown any indications of other than simple character.

The statements of Mendeleeff as to the possibility of tellurium containing another element, and his views as to its incorrect atomic weight, have led to an extended series of critical studies on this subject. Brauner studied the atomic weight for six years, Norris for nine, Baker and Bennet for thirteen, and the author for ten. We see, therefore, thirty-eight years of experimental work directed to the study of the atomic weight of an element which to-day remains as an element whose elementary character is well established, and which stands with a higher atomic weight than the next element in the horizontal series. While it still remains an exception to the periodic arrangement of Mendeleeff, and so far as its comparison with iodine is concerned, is abnormal, yet in the main points of its chemical behaviour and those of its compounds, it properly belongs associated with sulphur and selenium in the sixth group.

The element tellurium still remains, however, an exception to the periodic arrangement of Mendeleeff, its atomic weight being higher than that of iodine. We must hence conclude that either tellurium is abnormal in a direction which has not yet received careful study, or that we do not yet appreciate all of the principles of the periodicity of the elements. — *Journal of the American Chemical Society*, vol. xxx., No. 5.

RECENT DEVELOPMENTS OF THE KJELLIN AND ROCHLING-RODENHAUSER ELECTRIC INDUCTION FURNACES.*

By J. HARDÉN.

The object of this paper is to discuss the rapid development of the electric induction furnace during the last two years. Before proceeding to discuss the practical improvements in detail, it will be interesting to touch upon one or two novel points of a purely physical nature. We will consider one which will be of general interest.

The "Pinch" Effect of an Electric Current.

Many people experimenting with electric arc and resistance furnaces have observed that when a current is passed through a bath of molten metal or electrolyte the current density cannot be raised to a very high limit without distorting the bath. If the current density is raised to a certain point, it is plainly seen that the metal carrying the current contracts violently, or, in other words, becomes pinched, the effect of which is that the metal on either side of the pinch swells up above the average level of the bath. If the current is still increased, the pinch effect becomes so complete as to actually cause separation in the bath, thereby breaking the current circuit and causing a violent flash, together with rapid volatilisation. This is only a momentary effect, as the separate parts immediately flow together again, closing the circuit, when the same phenomenon repeats itself. Thus it was found impossible to pass an unlimited amount of power into the bath, although one might be well below the boiling-point of the metal. The explanation of this pinching is quite obvious. We have only to remember that conductors carrying current in the same direction have a mutual attraction for each other, and if we consider that the molten bath consists of an infinite number of elementary paths of current, it is natural that, as each one is attracting the paths in its immediate neighbourhood, there must be a tendency to compress the full section of the bath. If now, therefore, the bath is slightly contracted at any one spot, the current density will here be raised and the pressure

* A Paper read before the Faraday Society, June 23rd, 1908.

will increase until finally the bath becomes so pinched that an actual break in the circuit may take place. Of course this is only momentary.

Correspondents of the technical papers have discussed this question, and the point has been raised whether this phenomenon can also be observed in the induction furnace. Theoretically it is obvious that it should, for although the induced current is an alternating one, it has for a given moment of time the same direction in each part of the path.

We have taken observations under working conditions in a 60-kw. Kjellin furnace erected in London for experimental work. A small charge of pig-iron, consisting of about one-third of the full capacity of the furnace, was placed in the bath, and a current of 20 kw. was employed. As soon as the charge was fully liquid the pinching effect commenced, and the metal was seen to contract at a certain spot, raising the level of the metal on both sides of the pinch, which was sufficient to break the circuit, causing a flash, immediately after which the metal flowed together again, closing the circuit. The level of the metal immediately on each side of the pinched area rose about 1½ in. above the normal level of the bath. It was found, on examination, that a small piece of slag was burnt into the bottom of the hearth at the point where this phenomenon occurred, thus causing the original reduction of area. Pieces of pig-iron were added to the bath, and as the depth increased the pinching slowly disappeared. It was found that if the original charge was about half of the full charge no pinching effect could be observed.

Another striking feature is the resistance curve of the melt—that is to say, the curve obtained by taking the voltage across the terminals of the furnace during melting. Supposing we are starting the charge by meant of a cold ring of welded or cast-iron. Putting on a full load and keeping the kilowatts constant, we first find that the voltage rises above the normal for full load, and as the ring gets hotter the voltage still gradually rises until the ring becomes a bright red heat. From that point a decided drop in the voltage is noticed, although the power is kept constant and the weight of the charge is kept the same. As soon as the ring begins to melt the voltage again rises, but does not reach the same value as before the ring was red-hot. Now let us consider the cause of this result. This furnace is, as you know, nothing but a transformer with a short-circuited secondary. This latter must be placed some distance from the primary, owing to the thickness of the lining, cooling chamber, &c. We therefore have a certain amount of magnetic leakage, not only around the primary, but also round the secondary. The secondary is of iron, with comparatively high permeability, and we have therefore introduced an easy path for the lines of the stray field, hence the increased inductive voltage across the terminals. This is to a certain extent compensated for by the lower ohmic resistance of the ring; but as the resistive coefficient of the latter is such as to increase with the temperature, the total resistance, measured across the terminals, will increase with the temperature, but the power factor will be lower during this period, which shows that it is not only the ohmic resistance that is increased, but also the inductive resistance. This is due to the fact that the permeability of the iron is also increased to a certain extent with the temperature; in fact, it rises very rapidly up to a temperature of about 840° C., when the permeability begins to drop very quickly, and reaches zero at about 920° C. In this interval between 840° and 920° the inductive resistance is rapidly decreasing, because the easy path for the stray field is checked, and the voltage across the terminals is consequently lowered. But in the meantime the ohmic resistance is steadily increasing, but more slowly than the change in the permeability; therefore the voltage will again rise, though slowly, until the temperature is reached at which the loss by radiation and the heat introduced balance each other. It may even increase somewhat above this point, owing to oxidation of the charge, but this increase is very slight. This is the explanation why some people were misled into believing that the increase of resistance in iron due to heat was not a straight line curve. (It may, perhaps, not be so, but the effect shown on the furnace terminal is certainly produced in the way stated—which can be proved by the wattmeter readings).

Now, turning our attention to the more practical side of our process, we recognise a new feature, which is likely to prove a distinct improvement, viz., the Röchling-Rodenhauser modification of the induction furnace.

In the original Kjellin furnace some disadvantages are experienced when dealing with material which has to be refined and treated in very large quantities. For instance, when a charge of three tons or more is to be treated, the section of the bath becomes very large, thus causing a low resistance, whereby the power factor is lowered. If we try to increase the resistance by making the ring wider in diameter and of smaller section, the distance from the primary will be greater and the power factor again lower. Thus it becomes necessary to employ a generator of very low periodicity for such furnaces, which is, of course, undesirable. Also the processes of desulphurisation and dephosphorisation are very tedious, as it is difficult to keep the slag sufficiently liquid for such purposes. Nevertheless, this class of furnace will still hold its own, as it forms an almost ideal crucible steel furnace. In the case of crucible steel we have seldom to deal with more than one and a-half to two tons at a time, and as it does not pay to use impure raw material, no refining is required, but plain melting and "killing," and for this class of work plain induction furnaces can be provided, which will answer very well at 15 to 25 cycles per second. But when it is desired to refine, say, a material smelted from inferior ores and decarburised in a converter, but still containing up to 0·1 to 0·2 per cent cent sulphur and 0·05 or more phosphorus, in quantities of five to seven tons, this plain induction furnace would not be so satisfactory.

This was what was required for making rail and other similar steel at the Röchling'sche Iron and Steel Works at Völklingen, Germany, and therefore the engineers at these works, Mr. Rodenhauser and Dr. Schönawa, set themselves to adapt the Kjellin furnace, and so arrived at the "combined furnace." This consists of a transformer furnace with two ring-shaped baths adjacent and communicating with one another, in the case of a single-phase furnace, and three such baths in the case of a three-phase furnace, with a square or rectangular hearth in the centre between the rings, with doors in front and behind, in exterior appearance very much like a Siemens open-hearth furnace; but the principal feature is a heavy secondary winding of copper cables, placed around and conaxial to the primary (one on each leg of the core), surrounded by the rings forming the charge. These copper secondaries, consisting of a few turns only, are connected to conductive plates—they can hardly be called electrodes, for reasons given below—built into the furnace wall, two in front and two at the back for a single-phase furnace. These plates consist of corrugated cast steel plates, and a compound of magnesite, dolomite, and tar is applied firmly over the corrugation. The plates do not conduct well when cold, but as soon as the furnace is charged with molten raw material they will act as a "conductor of the second class," and readily allow the current to pass. Thus about one-half of the power is transmitted to the charge by induction in the rings and the rest of the power through the side plates. As the copper secondary is placed very close to the primary, the leakfield is very much smaller; in fact, three furnaces for one to one and a-half tons are now in operation with 50 periods at a power factor of 0·7 to 0·85, a result which could never be obtained with a plain induction furnace of a similar size, in spite of "bifilar" baths and other devices which have been tried. But *this* is not the chief advantage, as the same result may be obtained by other electrical means. A far more important gain is to be found in the metallurgical possibilities obtained with the new design. We know that for carrying out any

refining proeess in steel we need a sufficiently liquid slag, and ways and means of handling the same. This is to a certain extent obtained in some "electrode furnaces," where an arc plays between carbon blocks and the slag "blanket." This, however, in some cases, has proved troublesome, the drawback being that the temperature must be extremely and unnecessarily high at the spot where the arcs are playing, which is not without certain disadvantages to some steels. If we try to dip the carbons direct into the molten metal, we find that they are consumed at once, in such case contaminating the steel, which is, of course, difficult to avoid.

But this is not so in the case of the combined furnace. The conducting side plates before mentioned are of quite a neutral nature; in fact, some plates, which have been in constant use day and night for three months, were so little corroded at the end of that period that the loss of the plates, calculated per ton of steel, was hardly determinable. Part of the power is induced in the rings, thus heating the charge, and the rest passes through the side plates, to such an extent only as experience has proved to be necessary in order to obtain a sufficiently liquid slag. The ring-shaped part of the bath is covered with bricks, at a height below the level of the charge in the centre bath. Thus no slag can enter into the rings, and as it is the slag which is injurious to the lining, the rings need hardly any repair during a long run, whereas the rectangular bath in the middle is easily accessible, and can easily be patched out.

The lining is simply burnt magnesite or dolomite, mixed with tar, and stamped in hot.

It has been said that the use of these steel side plates would be equal to a return to the old system of electrodes, with all their disadvantages, but it is evident from what has been stated above that this is not so, as practically no consumption whatever of these plates takes place, and they can hardly be called "electrodes" in that sense of the word.

Let us now follow up the progress of the operation. After the lining is stamped in, the tar is burnt out (either by heating a cast steel ring or pouring a small quantity of pig-iron into the hearth), leaving behind a sintered mass, forming a solid brick of basic lining. The pig-iron is teemed for treatment in the Bessemer converter, and a fresh charge is given, which is tapped direct from the converter. It is more economical to burn out the carbon and the silicon in the converter before refining from phosphorus and sulphur. The larger furnace at Völklingen will take a charge of four tons.

Calcined lime is added to form a suitable slag; this slag also contains about 6 per cent of magnesia. Sometimes a small quantity of fluor-spar is also added to act as a flux, but this is not always necessary. Plate scale from the rolling-mill is added for decarburising.

In this condition the slag will take up the phosphorus very readily, after which it is made more viscous by applying cold lime, and drawn off through the slag door by a slight tilting of the furnace.

It is essential for a successful dephosphorisation that the charge should be what is called "hot brittle"—*i.e.*, have an excess of oxygen, in order to prevent the phosphorus wandering back into the charge again. After removing the slag which contains phosphorus, ferrosilicon or carbon is added, forming SiO_2 or CO, thus depriving the charge of the oxygen. It has been found that the adding of ferrosilicon will shorten the time of the deoxidation; thus, if power is cheap the cheaper carbon may be employed, and in the case of dearer power it is better to use the ferrosilicon.

As soon as the dephosphorising is effected this first slag is entirely removed, and a fresh slag of lime only is formed, which, when the temperature is raised, acts as a desulphuriser in forming iron sulphide. The oxygen is also driven out in this operation, partly by forming calcium carbide, and partly by adding a small quantity of ferrosilicon, and eventually some mill scale.

After this, the maximum power is given in order to drive out the last trace of oxygen, and as soon as no more gas bubbles are seen to leave the charge a test piece is taken out and forged. If too soft for the purpose, some coke powder is thrown in until the right proportions are arrived at. As a rule, the charge is finished in one and a quarter to two hours, but if necessary the steel can, without disadvantage, be kept in the furnace for ten hours or more. It is thus possible to treat a material which contains up to 0·1 per cent phosphorus and 0·1 per cent sulphur or more, so that a sulphur product containing 0·006 per cent phosphorus and 0·02 per cent sulphur, and from 0·5 to 0·1 per cent manganese and 0·01 silicon, will be obtained.

As to the power consumption, if the furnace is charged with molten material from the converter, the consumption is from 125 to 150 kw. hours per ton of finished material. This, of course, depends upon the quality of the raw material, but 130 kw. hours may be taken as a good average.

The finished product is especially distinguished by its great strength, equality, and homogeneity. In fact, rails have been made with a much higher bending and breaking point than ordinary Bessemer or Thomas rails, and these rails command from 25s. to 45s. per ton more than ordinary rails, owing to their greater durability. There is no necessity to give a large quantity of figures as to strength, &c., of this material, but a few may be useful.

Carbon	0·075
Phosphorus	0·03
Manganese	0·594
Sulphur	0·069
Silicon	—

Breaking sixty-four tons per square cm., elongation 21 per cent, contraction 28·5 per cent.

Carbon	0·086
Phosphorus	0·018
Manganese	0·310
Sulphur	0·077

Breaking 37·3 per cent, elongation 36·5 per cent, contraction 69·2 per cent.

Discussion.

Mr. F. W. Harbord, while holding the modified furnace to be a decided improvement on the original, doubted whether this type of electric furnace could compete against the modern converter or open hearth furnace for making rail steel. It was essentially a crucible furnace of large size. He was interested to note that CaC_2 was formed *in situ* in the furnace.

Dr. J. A. Harker said they hoped at the National Physical Laboratory to make determinations of some of the urgently needed physical constants of metals at high temperatures in the small experimental Kjellin furnace which had been presented to the laboratory. This type of furnace, in which metals could be melted in a neutral atmosphere, was ideal for the purpose. The new metallic filament lamps were greatly in need of a vacuum induction furnace.

Mr. E. Ristori remarked that it was necessary to fall back on the resistance principle as soon as the induction furnace was required to refine.

Alkaline Chloroiridates and Chloroiridites.—Marcel Delépine.—The chloroiridates of potassium, rubidium, cæsium, and ammonium can be obtained by double decomposition with the sodium compound, $IrCl_6Na_2+6H_2O$. Their general formula is $IrCl_6M_2$. The chloroiridites of sodium, potassium, and ammonium can be prepared by reducing the corresponding iridates in suspension, or dissolved in water by means of neutral oxalate, and warming on the water-bath. $2IrCl_6M_2+C_2O_4M_2=2IrCl_6M_3+2CO_2$. The salts of the type $IrCl_6M_3$ readily lose water, while the dimetallic salts, $IrCl_5(H_2O)M_2$, suffer no loss at 150°, and do not change colour; the water they contain is water of constitution.—*Comptes Rendus*, cxlvi., No. 24.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

Part III.—Analysis of the Aluminium and Iron Groups, including Beryllium, Uranium, Vanadium, Titanium, Zirconium, and Thallium.

By ARTHUR A. NOYES, WILLIAM C. BRAY, and ELLWOOD B. SPEAR.

(Continued from p. 17).

General Discussion (continued).

12. The filtrate from the chloric acid precipitate is first tested for phosphate. When it is not present, the iron, thallium, titanium, and zirconium are separated from the other elements by the addition of ammonium hydroxide. When phosphate is present, in order to separate it from the alkaline earth elements, the basic acetic precipitation is employed, ferric chloride being first added if necessary. The provision here made for the case that phosphate is present is thought to have many advantages over the methods ordinarily employed in schemes of qualitative analysis, where the phosphate is removed by tin in nitric acid solution, by ferric chloride and barium carbonate, or by ferric chloride and ammonium acetate in the first stages of the analysis of the group. Of these three processes, the basic acetate is much more rapid and simple of execution; but it does not give a separation which is at all satisfactory when applied to a solution containing all the elements of the aluminium and iron groups; thus chromium and zinc may in certain combinations of elements be found either in the precipitate or filtrate, and manganese also divides, unless great care is taken to make the precipitation in a large volume at the proper acid concentration. In the scheme of analysis here presented, this basic acetate separation has been introduced only after these troublesome elements have already been removed, for the presence of phosphate involves no complications in the preceding steps of the process. Under these circumstances it is no more difficult to secure accurate results in this separation than in the precipitation with ammonium hydroxide. Indeed, by adopting this process for all cases the complication of the alternative procedure and the special test for phosphate might be removed; but since the operations require a somewhat longer time, it has seemed best to retain the ammonium hydroxide precipitation for the case that phosphate is not present.

13. The iron might be separated from the titanium and zirconium by the well-known method of boiling a solution of the elements kept slightly acid with sulphurous acid; but it is difficult to secure complete precipitation of the titanium and zirconium and at the same time to prevent the carrying down of iron. Besides this, the operation is a long one, involves large dilution, and makes it necessary to use hydrofluoric acid in re-dissolving the precipitated hydroxides. On the other hand, the removal of the iron by the method of Rothe (*Stahl und Eisen*, 1892, xii., 1052; 1893, xiii., 333), which consists in shaking it out of a strong hydrochloric acid solution by means of ether, is extremely simple and rapid, gives a perfect separation, and leaves the titanium and zirconium in solution. We have therefore unhesitatingly employed this method in our scheme of analysis. Moreover, in this process the thallium, which is present as thallic chloride, is extracted together with the ferric chloride by the ether; it can be readily detected, after evaporating off the ether and reducing the ferric and thallic salts with sulphurous acid, by the formation with potassium iodide of the characteristic yellow precipitate of thallous iodide.

14. For the separation of the titanium and zirconium from each other we have adopted the process of Hillebrandt (*Bull. U.S. Geol. Survey*, 1900, No. 176, p. 75), which consists in adding sodium phosphate to a slightly acid solution containing hydrogen peroxide, whereby the zirconium is precipitated and the titanium remains in solution. The latter is shown to be present by the colour of the solution, but it can also be precipitated as phosphate by destroying the hydrogen peroxide with sulphurous acid after filtering off the zirconium compound.

15. The analysis of the ammoniacal solution containing nickel, cobalt, and perhaps zinc and the alkaline-earth elements, is carried out along the conventional lines. The first three elements are precipitated by the addition of ammonium sulphide, and the zinc is extracted, if the precipitate is large, by treating it with cold dilute hydrochloric acid, or if it is small by dissolving the precipitate completely and treating again with sodium peroxide. Instead of separating the nickel and cobalt from each other, it was found to be shorter and more conclusive to divide the solution of the sulphides into two parts and to test one portion for nickel by adding potassium cyanide and sodium hypobromite and the other portion for cobalt with potassium nitrite. The conditions for securing the best results in the nickel test were fully studied. Finally, in the filtrate from the ammonium sulphide precipitate the alkaline-earth elements are precipitated with ammonium carbonate as usual.

16. Though no provision is made in the system of analysis for the separate detection of any of the rare-earth elements, yet a process has been described for determining whether any of them are present and for removing them when they are found to be in the solution. This process consists in evaporating the acid solution of the original ammonium sulphide precipitate, adding to the residue hydrofluoric acid, and filtering. This converts the rare-earth elements completely into insoluble fluorides, and enables them to be separated from all the other elements of the aluminium and iron groups (except from a very large quantity of aluminium). When alkaline-earth elements are present, these are also precipitated as fluorides, wholly or in part, and are separated from the rare-earth elements by decomposing the fluorides with sulphuric acid, diluting, filtering off any akaline earth sulphates that separate, and precipitating the rare-earths in the filtrate with ammonium hydroxide. This process of isolating the rare elements has been worked out in the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology by W. C. Arsem and H. I. Wood, for use as a group separation in the "System of Qualitative Analysis including nearly all the Metallic Elements" (two parts of this System have already been published—see *Technology Quarterly*, 1903, xvi., 93, and 1904, xvii., 214; Chemical News, 1906, xciii., p. 134 *et seq.*).

17. Final confirmatory tests are given for almost all the elements; and much experimenting has been done on some of these tests in order to make them delicate and reliable; thus, this is true of the colour tests for aluminium and zinc made by igniting the oxides with cobalt nitrate, of that for chromium with hydrogen peroxide and ether, of that for nickel with H_2S in an alkaline tartrate solution, and of that for vanadium made by adding H_2O_2 to an acid solution; also of the precipitation test for uranium with potassium ferrocyanide. No satisfactory tests have as yet been found for beryllium or zirconium. Many, but not all, of these confirmatory tests will be found superfluous and will be omitted by the experienced analyst, except in cases where a very small precipitate or one of doubtful character is obtained; but they will, we believe, be useful to those unfamiliar with this scheme, and they serve, in the case of students, the educational purpose of making them acquainted with additional reactions of the elements in question.

18. It may be thought an objection to this scheme of analysis that it involves a number of manipulative operations unusual in qualitative analysis, such as heating in a closed bottle, saturating the acid-ether solution with hydrogen chloride gas (in the separation of aluminium and beryllium), filtering through an asbestos filter (in the separation of manganese), and shaking out with ether in the separation of iron from titanium and zirconium.

* From the *Journal of the American Chemical Society*, xxx., No. 4.

These operations, when they have been once executed, are found to be little if any more troublesome than the ordinary operations of precipitation and filtration. They are, moreover, mostly employed only in connection with the detection of the rarer elements, where the difficulties in finding any satisfactory method are so great that a little additional trouble is an insignificant factor. And finally, from an educational standpoint, they introduce the student to new kinds of processes, thus enlarging his knowledge and diminishing the force of the objection that the ordinary study of qualitative analysis is too limited in its scope.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 18th, 1908.

Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

(Concluded from p. 22).

152. "*Benzeneazo-2-pyridone.*" By William Hobson Mills and Sibyl T. Widdows.

An alkaline solution of 2-pyridone couples with benzenediazonium chloride to yield bright yellow 5-*benzeneazo*-2-*pyridone* (m. p. 210—212°), the constitution of which has been established by the following synthesis:—6-*Chloronicotinamide* (m. p. 210—211°) was converted by sodium hypobromite into 2-*chloro*-5-*aminopyridine* (m. p. 82—83·5°). This reacts with nitrosobenzene to form 2-*chloro*-5-*benzeneazopyridine* (m. p. 108—109°) which was converted by sodium methoxide into 5-benzeneazo-2-pyridone, identical with the above product.

3-Hydroxypyridine also couples in alkaline solution with benzenediazonium chloride, giving rise to *benzeneazo*-3-*hydroxypyridine* (m. p. 167—169°).

The preparation of 5-*amino*-2-*pyridone*, its characterisation by its *dibenzoate*, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_5H_3N{\cdot}O{\cdot}CO{\cdot}C_6H_5$ (m. p. 211—212°), and its production together with aniline by reduction of 5-benzeneazo-2-pyridone, were also described. The base was prepared in the two following ways:—1. From hydroxynicotinic acid by Curtius' method (*Ber.*, 1894, xxvii., 778); ethyl hydroxynicotinate (m. p. 149—150°) is transformed through the *hydrazide* (m. p. 310°) and *azide* (m. p. 139—140°) into *bishydroxypyridylcarbamide*, $CO(NH{\cdot}C_5H_3N{\cdot}OH)_2$, which gives rise to the base on hydrolysis. 2. From the above 2-chloro-5-aminopyridine by the action of sodium methoxide.

153. "*The Electrolytic Chlorination of the Salts of some Organic Acids.*" By John Kenneth Harold Inglis and Fred Wootton.

The authors have examined the products obtained by the electrolysis of solutions containing a mixture of potassium halide with the potassium salt of an organic acid. It was found necessary to protect the liquid from the reducing action of the hydrogen by means of a porous pot. The results varied with the temperature and type of electrode employed. In the case of a solution containing potassium benzenesulphonate and potassium chloride, to which most attention has so far been paid, tri- and tetra-chloro-*p*-benzoquinone were formed if the solution was kept hot and a platinum-foil electrode used. At the same time, evidence was obtained of the production of mono-, di-, and trichlorobenzenesulphonates, substitution in the nucleus having taken place. These substitution products have not yet been satisfactorily separated. In a similar manner, using potassium bromide, tetrabromo-*p*-benzoquinone was produced. A platinum-gauze electrode gave different products, which have not yet been investigated. Indefinite results were obtained with sodium benzoate, phenol, and *p*-nitrophenol. When iodide was used instead of chloride, no substitution was detected.

154. "*The Action of Nitrous Gases on Dicyclopentadiene.*" By Alexander Rule.

The author has investigated the crystalline products formed by the action of nitrous gases on a well-cooled ethereal solution of di*cyclo*pentadiene.

The gaseous products from the action of nitric acid on arsenious oxide bring about the formation of a mixture which, on separation by means of alcohol, was found to consist of the ψ-nitrosite and the dinitro-derivative of the hydrocarbon.

The ψ-nitrosite is insoluble in cold alcohol, but on boiling is gradually dissolved, being at the same time decomposed into two molecules of nitro*iso*nitrosodi*cyclo*pentadiene. Sodium methoxide acts on the ψ-nitrosite with the formation of *iso*nitromethoxydi*cyclo*pentadiene and sodium hyponitrite. The methoxy-derivative, on treatment with nitric acid, forms a brilliant blue ψ-nitrol, which is very unstable.

The dinitro-derivative is soluble in alcohol, and thus may be easily separated from the ψ-nitrosite. It forms characteristic crystals, which melt at 121°.

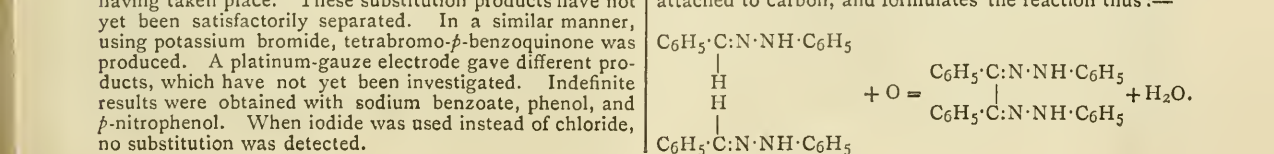
Sodium hydroxide acts on the dinitro-derivative, forming *nitrohydroxydi*cyclo*pentadiene*, which also forms a characteristic unstable blue ψ-*nitrol* with nitrous acid. The *sodium* salt of nitrohydroxydi*cyclo*pentadiene is obtained as a crystalline mass by cooling the alkaline solution, but the free hydroxy-compound shows very little tendency to crystallise.

155. "*An Alternative Structure for the supposed Stereoisomeric α-Osazones.*" By Frederick Daniel Chattaway.

By adding iodine to an ethereal solution of benzaldehydephenylhydrazone containing sodium ethoxide, Ingle and Mann (*Trans.*, 1895, lxvii., 606) obtained two isomeric substances of the formula $C_{26}H_{22}N_4$, melting at 186° and 208° respectively. The isomeride of lower melting-point was identified with diphenyldibenzylidenehydrotetrazone, first obtained by Minunni (*Gazetta*, 1892, xxii., [2], 217) by oxidising benzaldehydephenylhydrazone with mercuric oxide, and subsequently by von Pechmann (*Ber.*, 1893, xxvi., 1045), using amyl nitrite as the oxidising agent.

Ingle and Mann made the further observation that the second isomeride, melting at 208°, was transformed into ordinary benzilosazone on heating with various solvents. Entirely on the ground that stereoisomerides of benzilosazone were required by the Hantzsch-Werner hypothesis, they assumed that their newly discovered compound was one of these much sought for isomerides, and named it benzil-α-osazone. In order to determine its configuration, they heated both it and ordinary benzilosazone with cold concentrated sulphuric acid, and found that from the former only were they able to obtain, among other products, benzaldehyde. From this circumstance, they favoured the *syn*-configuration for the supposed new modification.

Biltz (*Annalen*, 1899, cccv., 165; cccviii., 1) discovered later that Ingle and Mann's benzil-α-osazone and a whole series of similar compounds could be obtained by dissolving the corresponding hydrazones in alcohol in presence of potassium hydroxide and oxidising them by a current of air. He observed that, like the first discovered compound, all these so-called α-modifications could be transformed by heat into the corresponding β-modifications derivable directly from the diketones. Biltz offers no evidence that these new compounds are stereoisomerides of the ordinary osazones, but accepts Ingle and Mann's assumption that this is the case; indeed, he seems to regard both isomerides as formed by direct removal of hydrogen attached to carbon, and formulates the reaction thus:—



Ingle and Mann in their paper record an observation which, properly interpreted, gives a far more likely explanation of this isomerism than that afforded by the Hantzsch-Werner hypothesis, and in this connection it should be noted that in no case has the third modification of these osazones predicted by this hypothesis been obtained. They show that the diphenyldibenzylidenehydrotetrazone obtained as one of the products of their reaction undergoes intramolecular re-arrangement into ordinary benzil-β-osazone on heating with alcoholic potash.

Now, this isomeric change of diphenyldibenzylidene-hydrazotetrazone into benzilosazone under the influence of alcoholic potash must without doubt take place in two stages, thus :—

$$C_6H_5\cdot N\cdot N:CH\cdot C_6H_5 \qquad C_6H_5\cdot NH\cdot N:C\cdot C_6H_5$$
$$\Big| \qquad\qquad \rightarrow \qquad\qquad \Big| \qquad\qquad \rightarrow$$
$$C_6H_5\cdot N\cdot N:CH\cdot C_6H_5 \qquad C_6H_5\cdot N\cdot N:CH\cdot C_6H_5$$

$$C_6H_5\cdot NH\cdot N:C\cdot C_6H_5$$
$$\rightarrow \quad \Big|$$
$$C_6H_5\cdot NH\cdot N:C\cdot C_6H_5,$$

and, in the absence of all evidence to the contrary, Ingle and Mann's benzil-α-osazone (m. p. 208°) ought certainly to be regarded as the intermediate product of this transformation. The presence of benzaldehyde among the products of its decomposition by sulphuric acid is direct evidence in favour of this view. The author has recently shown that hydrogen attached to nitrogen in aromatic hydrazines is attacked with extraordinary readiness by free oxygen (Chattaway, *Trans.*, 1897, xci., 1323), and his observations leave little doubt that the primary products when hydrazones are oxidised by air are hydrotetrazones, which thus undergo more or less complete transformation according to conditions. In Biltz's experiments, when the temperature is low, the first stage of transformation only occurs, the so-called α-osazones, which are really compounds of the general formula $\begin{matrix} R\cdot NH\cdot N:C\cdot R \\ \Big| \\ R\cdot N\cdot N:CHR \end{matrix}$, being formed; on the other hand, when the temperature is higher, the second stage of the transformation occurs, and the β-compounds result, these only being true osazones of the general formula $\begin{matrix} R\cdot NH\cdot N:C\cdot R \\ \Big| \\ R\cdot NH\cdot N:C\cdot R \end{matrix}$.

Baly, Tuck, Marsden, and Gazdar (*Trans.*, 1907, xci., 1579) have recently examined the absorption spectra of benzilosazone and its so-called α-isomeride. Finding them identical, they regard this as very striking and clear proof that the substances have the same configuration in solution. This appears to be a wholly unwarranted conclusion. Although such band absorptions, when different, may point to a difference of constitution, it can hardly be claimed that similarity of absorptions in such complex molecules as those in question can prove identity of configuration. To do this it would first be necessary to show that in presence of four phenyl groups a shift of one linking from nitrogen to carbon would produce an appreciable effect.

156. "*The Formation of 4-Pyrone Compounds from Acetylenic Acids.*" (Part II.). By SIEGFRIED RUHEMANN.

2-Phenyl-6-methyl-4-pyrone, which is formed by the action of sodium ethoxide on a mixture of acetone and ethyl phenylpropiolate (*Trans.*, 1908, xciii., 431), has been examined on lines similar to those which have been followed up by Feist (*Annalen*, 1890, cclvii., 253) in his work on dimethyl-4-pyrone. Under the influence of baryta, the former compound is transformed into *benzoylacetylacetone*, $C_6H_5\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot CO\cdot CH_3$ (m. p. 106—107°). This triketone does not condense with aldehydes in the presence of piperidine or alkalis as catalysts. It reacts with two molecules of phenylhydrazine to yield a colourless *substance*, $C_{24}H_{22}N_4$ (m. p. 174—175°), which only slightly reduces Fehling's solution on boiling, and which, most probably, has the constitution $\begin{matrix} N\cdot NPh- & & -NPh\cdot N \\ \| & C & \| \\ CPh\cdot CH_2 & & CH_2\cdot CMe \end{matrix}$ (see Feist, *loc. cit.*). With ammonia, the triketone condenses to form *2-phenyl-6-methyl-4-pyridone*, $CO<\begin{matrix} CH:CPh \\ CH:CMe \end{matrix}>NH$ (m. p. 177—178°), This compound is characterised by the fact that its aqueous solutions readily gelatinise. Several salts of the pyridone have been prepared.

157. "*The Fluorescence of Platinocyanides.*" By LEONARD ANGELO LEVY.

Barium platinocyanide exists in two forms, which exhibit a remarkable difference in their physical properties. One variety is golden-yellow and only very slightly fluorescent, the other variety being bright green and very fluorescent. The two forms are identical in crystalline character. The yellow salt is deposited from slightly acidified solutions, whereas the green form is best obtained by crystallisation from solutions containing a trace of barium hydroxide or barium cyanide. The experiments performed lead to the conclusion that the two forms have the same chemical composition, and are isomeric modifications. Similar phenomena are exhibited by the calcium salt, and to a certain extent by the cerium salt.

Barium platinocyanide, prepared from radio-active barium chloride, exhibits a strong luminosity, which is superior to that shown by a mechanical mixture of radio-active barium chloride and barium platinocyanide.

The property of fluorescence of a platinocyanide under the stimulus of radium radiations is usually exhibited in a marked degree by one hydrate form in particular. The others usually exhibit a feeble fluorescence or else show none whatever.

Certain regularities may be observed in the spectra of the fluorescence exhibited by platinocyanides of metals of the same group.

158. "*The Preparation of Disulphides.* Part II. *The Action of Alkalis on Sodium Alkyl Thiosulphates.*" By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS.

The interaction between alkalis and sodium ethyl and benzyl thiosulphates in aqueous solution has been studied. The chief organic product of the action in each case is the corresponding disulphide, the main step of the reaction being probably represented by the equation $R\cdot S_2O_3Na + NaOH = RS- + Na_2SO_3 + -OH$.

The RS— residues couple, in part, to give disulphide, whilst, at all events in the case of the benzyl compound, part of the RS— residues are oxidised, sodium benzyl thiosulphate giving appreciable quantities of benzoic and thiobenzoic acids.

The results were discussed in comparison with those of Gutmann (*Ber.*, 1908, xli., 1650), who, using alcoholic solutions, has arrived at a different view of the action.

159. "*Note on the Formation of Lead Ethoxide.*" By FREDERICK MOLLWO PERKIN.

When thin sheets of lead are boiled in alcohol or suspended in the vapour of boiling alcohol, no action takes place, but if they are suspended over absolute alcohol, and ozone is bubbled through it, in a short time the surface of the lead becomes tarnished, and then assumes a brownish yellow colour. At the end of some days, the whole of the lead is converted into a light yellow powder. On carefully washing this powder with alcohol and placing in an evacuated desiccator over sulphuric acid for some hours, a light yellow, friable powder is obtained. This, on analysis, proves to be *lead ethoxide*, $Pb(OEt)_2$. It appears to be soluble in water, although a clear solution is never obtained, probably owing to hydrolysis. It has not been found possible to obtain the ethoxide by passing oxygen alone through the alcohol, but, after the ozone has been passed for some time, the reaction can be completed by the continued passage of dry oxygen. When mercury is placed in alcohol and ozone bubbled through it, a white powder is formed which has not yet been analysed. The method is being tried with other metals.

160. "*Some Reactions of Phenylhydrazine with Metallic Cyanides and other Salts.*" By ROBERT DE JERSEY FLEMING STRUTHERS.

Phenylhydrazine in alcoholic solution combines with cuprous cyanide in ammoniacal solution to form an insoluble compound, $2CuCN,3C_6H_5{\cdot}NH{\cdot}NH_2$. This, superficially, closely resembles the compound obtained (*Proc.*, 1905, xxi., 95) by heating cuprous cyanide in an excess of phenylhydrazine, being similarly composed of shining scales, which gradually oxidise in air, and acquire a brilliant coppery sheen. These scales consist of microscopic crystals, the angles of which have now been successfully measured.

The substance readily decomposes on heating, nearly according to the equation :—

$$2(2CuCN,3C_6H_5{\cdot}NH{\cdot}NH_2) = 4CuCN+3N_2+3C_6H_6+3C_6H_5{\cdot}NH_2+3NH_3.$$

This, together with the previously described compound, $CuCN,C_6H_5{\cdot}NH{\cdot}NH_2$, co-ordinates with Moitessier's series of three compounds of phenylhydrazine with cuprous chloride, bromide, and iodide respectively (*Bull. Soc. Chim.*, 1899, [3], xxi., 666), and fills up the gaps, as below :—

$2Cu_2(CN)_2,4C_6H_5{\cdot}N_2H_3$; $2Cu_2Cl_2,5C_6H_5{\cdot}N_2H_3$, $2Cu_2(CN)_2,6C_6H_5{\cdot}N_2H_3$; $2Cu_2Br_2,7C_6H_5{\cdot}N_2H_3$. $2Cu_2I_2,8C_6H_5{\cdot}N_2H_3$.

Cobalt cyanide is found to exert a powerful catalytic action on phenylhydrazine, 0·03 to 0·04 grm. sufficing to determine the decomposition of 5 or 6 cc. of phenylhydrazine with almost explosive violence. The mixture is heated near its boiling-point for a short time until action is thoroughly established. The flame is then removed, but the action progresses with increasing intensity, and much evolution of heat, until the phenylhydrazine is completely decomposed. This catalysis by cobalt may be kept under control if only a few mgrms. of the cyanide are added to 4 or 5 grms. of phenylhydrazine, and the mixture distilled over paraffin, keeping the temperature carefully as low as 200°. In this way the evolved nitrogen may be easily collected and measured. The products appear to be principally aniline, benzene, ammonia, and nitrogen.

Nickel cyanide has a similar, but less, powerful action. Other salts of cobalt and nickel appear also to act more or less as catalysts. It seems possible that reduction may first occur, and the reduced metal be the true catalyst, although metallic nickel, not very finely divided, had only a slight effect. This action of cobalt is much more powerful than that of cuprous cyanide as described in the previous paper.

Other salts of copper have a strong catalytic action ; cupric chloride is nearly comparable with cobalt cyanide, and finely divided metallic copper (precipitated by iron) is fairly powerful as a catalyst. The acetate and sulphate, which deposit the metal as a mirror, are less powerful. Other metallic salts, such as lead and bismuth, seem to exert less action. In the case of lead acetate, a mirror of lustrous and coherent lead was deposited on the glass, resembling the copper mirror obtained by Chattaway, as described by him recently.

161. "*The Formation of Polyiodides in Nitrobenzene Solution.* Part III. *The Chemical Dissociation of the Polyiodides of the Alkali Metals and Ammonium Radicles.*" By Harry Medfordth Dawson.

A method has been devised by means of which the chemical dissociation in nitrobenzene solutions containing iodine and iodides of the alkali metals and substituted ammonium bases can be measured. This consists in the determination of the composition of the aqueous solutions which are in equilibrium with nitrobenzene solutions containing known quantities of iodide and iodine ; from relationships which have been previously established for aqueous iodide-iodine solutions, the concentration of the free iodine in the aqueous solutions can be calculated, and from this the concentration of the free iodine in the nitrobenzene solutions is obtained.

It was shown that polyiodides of the types MI_9, MI_7, MI_5, and MI_3 exist in nitrobenzene solutions, and that these represent the successive steps in a dissociation phenomenon in which iodine is the other product of dissociation. In solutions of the same molar concentration, the polyiodides of the different alkali metals and ammonium bases are chemically dissociated to the same extent ; this is probably due to the fact that the polyiodides are largely ionised, and the iodine resulting from the dissociation of a complex iodine ion which is common to the various polyiodides. Whereas the higher polyiodides are chemically dissociated to a considerable degree, the tri-iodides are very stable, and are but very slightly dissociated.

162. "*The Hydrolysis of Amygdalin by Emulsin.*" (Part II.). By Samuel James Manson Auld.

By observation of the change of rotation of the dextrose produced during the hydrolysis of mandelonitrile glucoside by emulsin, and the approximate constancy of the rotation after hydrolysing amygdalin by emulsin, it is possible to show that amygdalin is derived from an $\alpha\beta$-disaccharide, the β-dextrose residue being attached to the benzaldehyde-cyanohydrin nucleus.

Exact measurement of the quantities of hydrocyanic acid, benzaldehyde, and dextrose formed from amygdalin shows that mandelonitrile glucoside is formed as an intermediate product during the hydrolysis by emulsin, the biose ether-linking breaking preferentially. By stopping the hydrolysis at a suitable point, it is possible actually to isolate Fischer's glucoside.

163. "*A New Form of Potash Bulb.*" By Arthur Edwin Hill. (Will be inserted in next issue).

CORRESPONDENCE.

THE RECENT LETTERS OF THE HONORARY SECRETARIES OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

Sir,—The Fellows of the Chemical Society have recently received two circular-letters signed by the Honorary Secretaries. The motive of the letters has been, primarily, the reception by the Council of a petition for the admission of women to the Fellowship. It is not with the object of supporting that petition, which I have signed, that I write this letter, but in the hope of helping to stop the further issue of letters such as these over the official signatures of the Society's Honorary Secretaries.

The first of the two letters was authorised by the Council ; but it may be confidently assumed that had the Council foreseen how that letter would be composed, it would not have adopted it. It must by this time be evident, even to the members present at the last Council Meeting, that, as carried out, the resolution to issue to the Fellows, not a copy of the petition, but a statement instead of arguments for and against the admission of women, has proved itself to be unwise. We are told that the petition was not sent out, for fear that it might bias the opinion of Fellows—as though the Council had jurisdiction over the opinions of the Fellows, and with it the duty of guarding these opinions from being made other than a reflex of its own.

Half the Members of Council had signed the petition, yet those who had the ear of the meeting persuaded it to withhold the petition from the Fellows, on the ground that it was calculated to gain their adhesion to the movement—as, indeed, and quite properly, it was. I will not believe that, in saying that the petition would "bias" the opinion of Fellows, the Honorary Officers, in the second letter, meant to impugn the honorable and open character of a petition signed and supported by numbers of eminent chemists. Thus, inadvertently without doubt, the Council meeting passed a resolution calculated to affect unfavourably the votes of the Fellows, by withholding the petition from them. Before, therefore, the request to the Fellows for their votes had gone out, the opponents of the measure

had gained an unfair advantage, and they managed to gain still more.

The adoption of the alternative, that of sending out a statement of arguments on both sides, made the Council responsible for a still more seriously objectionable action by its Secretaries, for, as already pointed out, the Council can claim no right to bias or influence the opinions of the Fellows, or to submit to them a partial statement concerning a petition it has seen fit to act upon. The Council is responsible—but hardly perhaps to blame—for what was done; yet surely the meeting might have recognised the moral impossibility of an impartial statement being drawn up by men so strongly biassed and so active in opposition as the Honorary Secretaries were known to be. The consequence of this mistaken trust in the capacity of its Secretaries to carry out a delicate commission is already well known. The Secretaries omitted half the preamble of the petition. They said that the petition was for an inquiry, but they left out that it rested on the opinion that the time had come when the Fellowship of the Society should be rendered accessible to women. That is the published opinion of half the members of the Society's Council and of very many chemists of repute besides, yet the Fellows were to be left in the dark as to that. The serious consequence of this mangling of the preamble is emphasised by the circumstance that the statement had already been circulated, that many who had signed the petition had done so only for an inquiry, and not from a conviction that women should be eligible for the Fellowship. It cannot be pleaded that the Secretaries had not in mind the insertion of the preamble or any part of the petition in their letter, for in the second letter they give the latter half of the preamble within inverted commas, still leaving out its first half.

For issuing to the Fellows a statement of the arguments for admitting women to the Society, the Council Meeting had the petition in its hands to offer in justification of its action. But what had it to justify its sending out arguments against admitting women, not advanced by itself; but by "those who are unwilling" to admit women? From whom had the Council Meeting obtained official cognisance of the nature of these arguments? It had received no counter petition, and it did not itself advance these arguments. Did the Council, when acceding to the request of the petition to appeal to the Fellows, act constitutionally in publishing against the object of the petition arguments which it had not itself official knowledge of and had not endorsed? In any case, did it not, by issuing these statements of unindicated and unknown persons, act prejudicially towards the object of the petition, without finding it to be its duty to directly oppose that object. Still, again, advantage was given to the opposition by the Meeting's resolution to submit arguments for and against, instead of the petition itself.

The second letter, the receipt of which has led me to write this protest, cannot be denounced in the terms it deserves, since it is signed by all the Honorary Officers, including the President, whose impartiality is above suspicion. As the Fellows know, what led up to the publication of that letter, dated July 8th, was the letter to the Fellows from eleven Members of Council, Past Presidents of the Chemical Society. The Fellows, whatever view they may each hold on the subject of the Fellowship, must certainly feel greatly indebted to these Past Presidents, as also to Sir Henry Roscoe for his letter to *The Times*, July 3rd, to Professors Dixon and Perkin for theirs to the *Manchester Guardian*, July 4th, and to the writer of the article in *Nature* of July 9th, for putting the petition or the substance of it before them. The Past Presidents, it is to be noted, date their letter from Oxford, sign it without titles, word it most modestly, and make no reflection in it upon the action of the Council.

The Honorary Officers have thought it right to write to the Fellows from the Offices of the Society, with official signatures, and with the formality of an authorised communication from the Council, a letter charging the Past Presidents with having adopted a course unauthorised by the Council, and in direct opposition to a resolution passed by it, and to have done this in a way which might well have led Fellows to conclude that the Council had authorised their procedure. It is difficult to realise that such an apparently insulting and, at the same time, absurd charge against eleven most eminent and honoured chemists and Members of the Council has been made by the Officers, and, of course, it could not have been meant to be what, literally taken, it is. The Officers, we know, had no authority to write the letter as Officers of the Society; on the other hand, the Past Presidents' letter is not, on any possible view of it, open to the charge of assuming or claiming any authority but their own. What must have been the frame of mind of the Secretaries when writing a letter to the Fellows not only implying that the Past Presidents, in publishing the petition, required the authority of the Council or its Officers for this most serviceable and important action, but also representing that the Past Presidents had issued the petition in a way liable to lead to the belief that their action had the authority of the Council, regardless of the facts that the covering letter was dated from Oxford, and that the signatures without titles were those of universally known and respected and honourable gentlemen.

Everyone recognises the chemical ability and the estimable qualities of the Honorary Secretaries, but there are some who are now expressing doubt whether they should be fully entrusted with the writing of the Council's letters.—Iam, &c.

EDWARD DIVERS.

London, July 14, 1908.

PROPOSED ADMISSION OF WOMEN TO THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

THE following letter has been sent to all Fellows of the Chemical Society:—

Chemical Society,
Burlington House, London, W.
July 8th, 1908.

DEAR SIR,—You have doubtless received a letter emanating from Oxford and dated July 1st, enclosing a circular copy of the petition recently presented to the Council of the Chemical Society requesting the Council "to take such steps as may appear desirable to ascertain the wishes of the Society as a whole in regard to this question."

The envelopes enclosing the above communications bore the familiar printed address-slips which might well lead Fellows to conclude that they were issued by authority of the Council. This is not the case.

The Council resolved that the statement of arguments on both sides which was issued to Fellows on June 23rd, was better calculated to elicit the unbiassed opinion of all Fellows if sent alone.

The course adopted by the signatories of the Oxford Circular of July 1st is therefore not only unauthorised, but is in direct opposition to a resolution of the Council of which the signatories are members.—We are, Dear Sir, Yours faithfully,

(Signed) WILLIAM RAMSAY, President
HORACE T. BROWN, Foreign Secretary.
ALEXANDER SCOTT, Treasurer.
M. O. FORSTER, ARTHUR W. CROSSLEY } Secretaries.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 6th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Lady Low and Mr. H. N. Middleton were elected Members. The Special Thanks of the Members were returned to Mr. Oswald Lewis for his donation of £5 5s. to the Fund for the Promotion of Experimental Research at Low Temperatures.

THE CHEMICAL NEWS.

Vol. XCVIII., No. 2539.

THE LIQUEFACTION OF HELIUM.

We are now in a position to give the corrected version of the achievement of Professor Onnes, which carries with it the explanation of his wish for delay in publication. On July 14 he announced the liquefaction of helium in the following telegram, which was placed at our disposal by the courtesy of Sir James Dewar, who replied with "hearty congratulations on splendid achievement" :—

Leiden, July 14.

Dewar, Royal Institution, London.

Obtained 10 July 60 cubic centimetres liquid helium. Lasted for two hours. Not solid at two millimetres vapour pressure.

Kamerlingh Onnes.

On July 15 Professor Onnes telegraphed as follows, and also *ex abundante cautela*, telegraphed directly to ourselves, as already stated, a request for delay of publication :—

Leiden, July 15.

Dewar, Royal Institution, London.

Hearty thanks. Will give you great satisfaction to see considerable part joint to Van der Waal's theory your methods take in success, but please wait publication *Times* till last controls are ready.

Kamerlingh Onnes.

On the 18th, having verified his results, and probably repeated his experiment, he gave his final version in the following telegram :—

Leiden, July 18.

Dewar, Royal Institution, London.

Please change two millimetres into one centimetre; can then be published in *Times*. Boiling-point 4·3.

Kamerlingh Onnes.

Professor Onnes has therefore shown that helium is a liquid having a boiling-point of 4·3° absolute, which is not solid when exhausted to a pressure of 10 millimetres of mercury, at which pressure the temperature must have been reduced to within 3° of the absolute zero—*i.e.*, about one-fourth of the temperature of hydrogen in corresponding conditions, as that again is about one-fourth of the corresponding nitrogen temperature. If we could obtain another similar drop by the discovery of a gas still more volatile than helium we should have a liquid boiling about 1° above the absolute zero.

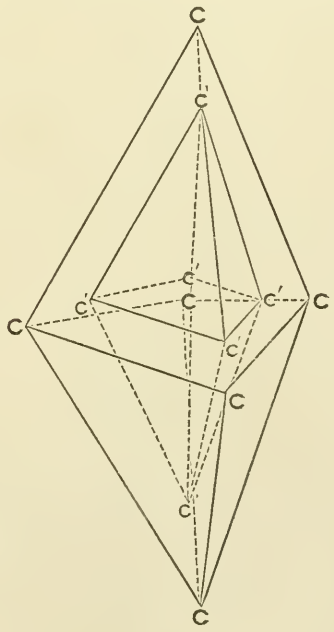
A few notes upon the steps by which the liquefaction of helium has been reached may be of interest. In 1895, by the application of the method of sudden expansion from high compression, Olscevski, starting from the temperature of exhausted air, failed to get any appearance of liquefaction. In 1901, Dewar, in the Bakerian Lecture, described his repetition of that experiment, using liquid hydrogen under exhaustion instead of liquid air, again without obtaining any trace of condensation. Reasoning from the analogy of his experiments on the liquefaction of hydrogen, he showed that by regenerative cooling starting from the temperature of liquid hydrogen, we might expect to liquefy a gas whose boiling-point might be as low as 4° or 5° absolute. In his Presidential Address to the British Association in the following year he gave reasons for placing the boiling-point of helium at that figure, showing at the same time how great are the experimental difficulties of getting within 5° of absolute zero. In 1905, Olscevski repeated Dewar's experiment of 1901, using higher pressures, and reached the conclusion that the boiling-point of helium must be below 2° absolute, and that after all the gas might be permanent. The same experiment was repeated early in 1908 by Professor Onnes with a much larger quantity of helium than had previously been available, and at first thought he had obtained solid helium, but found that the appearance was due to impurity in the gas. Dewar again repeated the experiment by circulating helium in a regenerative apparatus, but though he got cooling, he was baffled by the inadequacy of his supply of helium to maintain the cooling process sufficiently long to reach liquefaction. At last, by the experiment of July 10, Professor Onnes has definitely settled the matter. As new and richer sources of helium have been discovered, and its separation has been enormously facilitated by Dewar's charcoal method, it is possible that helium may become sufficiently abundant in cryological laboratories to be used as liquid hydrogen is now used in physical research.—*The Times*, July 20.

THE CONSTITUTION OF THE CARBON MOLECULE.

By J. C. THOMLINSON, B.Sc.

In the Chemical News of Jan. 24th (vol. xcvii., p. 37) I noted a critique of Sir James Dewar's suggested formula for the constitution of the carbon molecule.

I do not go into the question of the reasoning which in a former paper, Jan. 6th, 1906 (Chemical News, xciii., p. 37), and succeeding issues, lead me to give suggested heats of combination for carbon and other elements as distinct from the heat they evolve on union with oxygen or the heat of combustion, I would merely call attention to the accompanying diagram as representing a twelve



atom molecule of carbon as it might actually occur in space.

Without actually giving the geometric form of the system to which the diamond belongs, it will be seen that two solid figures, one enclosed within the other, and each containing six solid angles, could easily represent the position of twelve atoms of carbon which form the molecule.

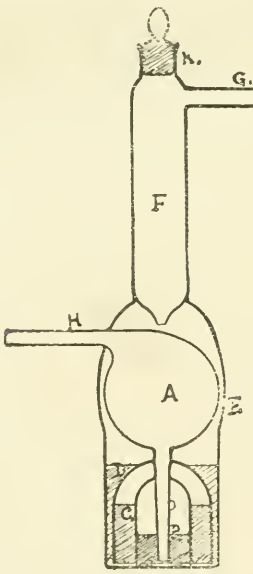
Such a figure comes within the terms of the description of the formation of the carbon molecule from two benzene nuclei as described in the above-mentioned critique, for we can easily imagine either of the solid figures given as formed from a benzene molecule by the elimination of the hydrogen atoms with the strengthening of the bonds of valency of the carbon atoms among themselves, these valencies being represented by the sides of each solid figure respectively.

Note.—Intramolecular tension mentioned in the article already quoted in connection with the discrepancies in the results of theory and practice would in the spacial formula given be accounted for by any force (physico-chemical) acting between the carbon atoms other than that represented by the usual valency bonds.

A NEW FORM OF POTASH BULB.*

By ARTHUR EDWIN HILL.

The potash bulb indicated in section in the figure consists essentially of the inlet tube A B, made up of the bulb A, and its lower extension the narrow tube B, which extension is surrounded by, and fused to, the glass domes C and D. Enclosing these is the outer vessel E, to which H, the upper part of the inlet tube, is fused. The exit tube F, which is drawn off at its lower end to serve as a receptacle for holding soda-lime, is fused to the top of the vessel E, and provided with a ground stopper K, and side outlet tube G.



To prepare the potash bulb for use, the ground stopper K is withdrawn, and a small plug of glass-wool is inserted and pushed to the bottom of the tube F. Recently ignited soda-lime, free from fine particles, is then poured into the tube until it is three parts full, and the remaining space is filled with small granules of calcium chloride; a small plug of glass-wool is inserted at the top, and the ground stopper is replaced. One such filling will last for at least twenty experiments.

The bulk of the carbon dioxide is absorbed with a concentrated solution of potassium hydroxide, which is contained in the vessel E, and renewed after every experiment. Any residual traces of carbon dioxide are removed by the soda-lime in the tube F, which also assists the calcium chloride to desiccate the gases before they leave the potash bulb.

A special feature of the potash bulb, which makes it very efficient, is the introduction of the domes C and D, which cause the gases to bubble through the potash solution three times in succession before they can come into contact with the soda-lime in the tube F.

After the gases have entered the bulb A, they pass down the narrow tube B, and bubble up through the solution into the dome C; they leave this through two holes in its wall, and bubble up through more solution into the outer dome D, which they then leave through two holes to enter the outer vessel E, after bubbling through the solution surrounding the dome D.

The position of these holes is so arranged that the gases must bubble through at least a quarter of an inch of potash solution each time; sufficient solution must be introduced into the potash bulb to cover the top of the dome D when the gases are bubbling through the solution. The section of the dome D is made elliptical in order to increase the quantity of solution adjoining the holes through which the gases bubble.

Although this bulb was designed for absorbing carbon dioxide, it can also be used for absorbing water vapour. For this purpose, the tube F is filled with granulated calcium chloride, and concentrated sulphuric acid is substituted for potassium hydroxide solution in the vessel E.

This new form of potash bulb presents a number of advantages.

1. A treble scrubbing action, which ensures a very complete absorption by means of a comparatively small quantity of liquid absorbent, supplemented by a final scrubbing with soda-lime and calcium chloride, which also ensures complete desiccation.

2. It is very compact and strong, being free from most of the weaknesses which characterise many of the potash bulbs now in use. It is easily manipulated, and will stand on its own base.

3. It can be easily and rapidly wiped dry before it is weighed, and will therefore give thoroughly concordant results, which are not affected by the amount of moisture in the surrounding air.

(We are indebted to the author for permission to use the woodcut illustrating this Paper).

* Abstract of a Paper read before the Chemical Society, June 18, 1908.

DETERMINATION OF NICKEL AND CHROMIUM IN STEEL.

By EDWARD DeMILLE CAMPBELL and WALTER ARTHUR.

In February, 1895, one of the authors in conjunction with W. H. Andrews, published a method for the determination of nickel in nickel steel (*Journ. Am. Chem. Soc.*, xvii., 125), in which the nickel was determined electrolytically or by titration with potassium cyanide, using silver iodide in suspension as an indicator. About six months later Thomas Moore published his article "The Volumetric Estimation of Nickel" (Chemical News, lxxii., 92), in which he showed that the use of silver iodide as an indicator renders the cyanide titration of nickel sharp and accurate. Credit for the cyanide titration of nickel by the use of silver iodide as an indicator is usually given to Moore, and undoubtedly this modification was worked out independently. In most of the materials analysed by Moore the proportion of iron to nickel was comparatively small. He makes the statement towards the latter part of his article that "In presence of alumina, magnesia, or ferric oxide, citric acid, tartaric acid, or pyrophosphate of sodium may be employed to keep them in solution."

A number of volumetric methods based upon the cyanide titration of nickel using silver iodide as an indicator have appeared since the above was published. Most of these methods aim either to remove the iron before titrating for nickel or to add some reagent which will keep the iron dissolved when the solution is rendered alkaline.

H. Brearley (Chemical News, lxxiv., 16) precipitates the iron in rather strongly acid acetate solution as basic acetate, and titrates the nickel in an aliquot part of the filtrate, while G. T. Dougherty (*Iron Age*, April 25, 1907) precipitates iron as ferric hydroxide by means of a large excess of ammonia in presence of a strong solution of ammonium chloride. His results seem to show that if sufficient ammonium chloride be added, the ferric hydroxide will not contain any nickel, so that the titration of the aliquot portion of the filtrate will give accurate results.

As early as 1899, G. W. Sargent (*Journ. Am. Chem. Soc.*, xxi., 854) described a combination of the now well-known ether method for the separation of iron with the cyanide-iodide titration for nickel. This combined method has been quite satisfactory in many ways, but where a large number of determinations are being made, the expense of the ether, combined with the danger of fire attending its use and the disagreeable effect of inhaling the vapours, render the use of the ether method not entirely satisfactory.

The latest modification of the cyanide-iodide method for nickel in steel is that proposed by C. M. Johnson (*Journ. Am. Chem. Soc.*, xxix., 1201). Johnson describes the cyanide-iodide method as that of T. Moore, although this method appeared in this country some six months in advance of the latter's article.

In the method proposed by Johnson, which is a modification of that given by Brearley and Ibbotson in their "Analysis of Steel Works Materials," p. 183, the iron is kept in solution in the presence of a little free ammonia, by means of a large amount of citric acid, instead of a small amount as recommended by the above authors. By using 12 grms. of citric acid per grm. for ordinary nickel steels and 24 grms. in case of chrome-nickel steels, the colour of the solution is rendered light enough to observe the silver iodide without difficulty.

Johnson has shown that the amounts of vanadium, tungsten, molybdenum, and manganese found in commercial steels do not interfere with the titration of nickel, and that the dark colour due to the presence of chromium may be partially overcome by the use of an increased amount of citric acid.

Experiments made in the laboratory of the University of Michigan with the method described by Johnson showed that even in the presence of large amounts of ammonium citrate, the brownish colour of the ammoniacal solution did not permit as satisfactory a titration of nickel to be made as desired. We have endeavoured therefore to see whether the use of sodium pyrophosphate to keep iron in solution would not give better results than the ammonium citrate.

In his original publications, Moore gave no details concerning the use of sodium pyrophosphate, since in the materials on which he worked the amount of iron present was not large enough to cause any trouble. In applying the method to the analysis of steel, some care is required to obtain conditions, such that the colour of the solution will not be dark enough to cause any uncertainty as to the end reaction. The following method has been worked out, and found to give satisfactory results in this laboratory :—

One grm. of the steel is dissolved in a casserole with 10 to 15 cc. of nitric acid (sp. gr. 1·2) with the addition of a little hydrochloric acid if necessary. After solution of the steel, 6 or 8 cc. of sulphuric acid (1:1) are added, and the solution is evaporated until the sulphuric anhydride fumes begin to come off. Thirty to 40 cc. of water are now added, and the solution heated nearly to boiling or until the ferric sulphate is all dissolved. The solution is then transferred to a 400 cc. beaker. In case the solution in the casserole is not perfectly clear but contains a little silica or carbon in suspension, it should be filtered so that the solution in the beaker is perfectly clear and bright. To the sulphuric acid solution in the beaker, which should be about 60 or 70 cc. in volume, are added 13 grms. of sodium pyrophosphate previously dissolved in about 60 or 70 cc. of water heated to about 60° or 70°. After the addition of the sodium pyrophosphate, the solution containing the heavy white precipitate of ferric pyrophosphate is cooled to room temperature, and dilute ammonia (1:1) is added drop by drop, while the solution is vigorously stirred, until the greater portion of the pyrophosphate has dissolved, and the solution has assumed a greenish tinge. The solution at this point should have an alkaline reaction towards litmus, but it should not smell of free ammonia. The solution is now warmed gently, and stirred, when the remaining pyrophosphate will competely dissolve, giving a perfectly clear light green solution. If the ammonia is added too fast or the solution is not carefully stirred, a brownish colour is apt to result, but this can usually be overcome by carefully adding a few drops of dilute sulphuric acid. The clear light green solution is now cooled to room temperature, and 5 cc. of silver nitrate (made by dissolving 0·5 grm. of silver nitrate in 1000 cc. of water) are added, followed by 5 cc. of a 2 per cent solution of potassium iodide. Standard potassium cyanide is now run in until the clearing up of the solution shows that the nickel has been completely converted into potassium nickel cyanide and the silver iodide into potassium silver cyanide. Before calculating the amount of nickel present, correction must be made for the amount of potassium cyanide required for the 5 cc. of indicator used.

The potassium cyanide used may be decinormal, made by dissolving about 13 grms. of potassium cyanide in 1000 cc. of water, and standardising by direct titration with standard decinormal silver nitrate. If decinormal potassium cyanide is used, since the titration of the nickel takes place according to the equation $NiSO_4 + 4KCN = K_2Ni(CN)_4 + K_2SO_4$, the decinormal factor of metallic nickel will be 0·002935. If preferred, the potassium cyanide may be standardised against a nickel solution of known strength.

The above method gives very satisfactory results with nickel steels not containing chromium or copper.

If copper is present in amounts not exceeding 0·4 per cent, the amount of potassium cyanide required for the copper will not be as great as it would for an equal per cent of nickel, but the copper will replace almost exactly three-quarters of its weight of nickel. Thus, if a sample contained 0·12 per cent of copper, it would require an amount of potassium cyanide equivalent to 0·09 per cent of nickel. In almost all cases of nickel steels containing copper, if the sample is dissolved in a covered Erlenmeyer flask in 25 cc. of water to which is added 5 cc. of sulphuric acid (sp. gr. 1·84), the nickel will all go into solution, and the copper will remain undissolved. The solution is cooled, and the undissolved copper is filtered out. The ferrous sulphate in the filtrate is oxidised by the addition of a slight excess of hydrogen peroxide, and the excess of this latter is boiled off. The solution is concentrated if necessary, and the method continued as in the case of nickel steel containing no copper.

In the case of chrome-nickel steels the sample is dissolved and converted into sulphate as described in the first method. After dissolving in the casserole in about 40 to 50 cc. of water, the solution is brought to boiling and a 2 or 3 per cent solution of potassium permanganate is added drop by drop to the boiling solution until a slight permanent precipitate of manganese dioxide is obtained. The chromium in this way is readily oxidised to chromic acid much as in the well-known Galbraith process for the determination of chromium. The solution is now cooled to room temperature, filtered, and the filtrate and washings concentrated in a 400 cc. beaker to about 60 cc. Sodium pyrophosphate is added, and the process continued as in the first instance when chromium is not present. By oxidation of chromium to chromic acid, the dark colour due to the presence of chromic salts is avoided, and the chromic acid takes no part in the titration of the nickel. The clear solution to which silver nitrate is added, will have a yellow rather than a green colour when chromium is present, but no trouble is experienced in obtaining a sharp end reaction.

In case of chrome-nickel steels, the chromium may be advantageously determined in the same sample as that used or the determination of the nickel. The solution of the

sulphates in which the chromium has been oxidised to chromic acid, must be cooled thoroughly before filtering if filter-paper is used, in order to avoid any reduction of the chromic acid by the paper. To the clear solution of the sulphates containing chromic acid, an accurately weighed amount, usually 0·7 grm., of ferrous ammonium sulphate is added, and the excess of ferrous sulphate oxidised by means of standard potassium permanganate.

In order to obtain an accurate titration by means of potassium permanganate in the presence of chromic sulphate, it is best to weigh out the ferrous ammonium sulphate and reserve a small portion to be added after the pink colour of the permanganic acid, usually indicating the end reaction, has been obtained. The reserved portion of the ferrous ammonium sulphate is then added, and the titration continued, employing, however, potassium ferricyanide as an external indicator as in the titration of iron by means of potassium dichromate. Since the green chromic sulphate is partially complementary to the red permanganic acid, the colour of this latter which usually indicates the end reaction will not be visible until too large an excess has been run in. From the weight of the ferrous ammonium sulphate used and the amount of the decinormal potassium permanganate required, the per cent of chromium may be readily calculated as in the well-known methods for the volumetric determination of this element. When chromium has been determined, the solution is again brought to the boiling-point, and the chromium again oxidised to chromic acid by the addition of a 2 per cent solution of potassium permanganate until a slight permanent precipitate of manganese dioxide is obtained. The solution is again cooled until cold, and the manganese dioxide filtered out, and the method continued as though the chromium had not been determined. If more than 1 grm. of ferrous ammonium sulphate has been used, 1 or 2 grms. additional sodium pyrophosphate should be added.—*Journal of the American Chemical Society*, xxx., No. 7.

THE ACTION OF HYDROGEN SULPHIDE ON ALKALINE SOLUTIONS OF ZINC SALTS.

By L. W. McCAY.

THE fact that the zinc sulphide, or the zinc hydrosulphide, precipitated from alkaline solutions of zinc salts by sodium or potassium hydrosulphide is soluble in an excess of these reagents, and that the zinc sulphide, or zinc hydrosulphide, precipitated from alkaline solutions of the metal by hydrogen sulphide dissolves when the gas is permitted to act on the solutions for some time, appears to have escaped the notice of the analytical chemists.

NOTE.—I noticed this peculiar behaviour of zinc sulphide some three or four years ago, and supposed that my observation was a new one. I found, however, that the reaction was first observed by Julius Thomsen in 1878 (*Ber.*, xi., 2044) and subsequently examined by A. Villiers (*Comptes Rendus*, cxx., 97). Lottermoser ("Samlung chem. u. tech. Vorträge," VI.) and Winsinger (*Bull. de l'Acad. des Sciences de Bruxelles*, [2], xiv., 321) also refer to it.

At all events, in no work on analytical chemistry to which I have access is this remarkable behaviour of zinc sulphide referred to. The solution of the zinc sulphide is a colloidal one, for the zinc in it will not pass through parchment paper. The zinc sulphide, or zinc hydrosulphide, acts towards sodium and potassium hydrosulphides in much the same way that zinc oxide, or zinc hydroxide, acts towards sodium and potassium hydroxides. The analogy between the two reactions almost compels one to conclude that the change takes place in the sense of the equation $Zn(SH)_2 + 2RSH = R_2ZnS_2 + 2H_2S$.

If, however, an alkali sulphozincate is actually formed, t must be very unstable, for concentrated solutions of mineral salts, when added to its solution, precipitate only zinc sulphide, or possibly zinc hydrosulphide; and then too the zinc sulphide separates out gradually, and in a slimy condition, when the solution is allowed to stand.

In many books on qualitative analysis the student is directed to separate manganese from zinc by adding to the solution of their chlorides an excess of sodium or potassium hydroxide. Now if the alkaline solution of the zinc, after its separation from the manganous hydroxide, be treated for fifteen to twenty minutes with a rapid current of hydrogen sulphide, the zinc sulphide which is first precipitated may dissolve. The smaller the amounts of zinc and sodium chloride present in the solution, and the more rapid the current of gas, the more readily does the zinc sulphide formed pass into solution. Should a student pass a rapid current of hydrogen sulphide into such a solution, and then leave the spot and not return until after the lapse of some fifteen to twenty minutes, the chances are he will find the solution clear, or nearly so, and report no zinc. I have convinced myself by a number of experiments that there is, in a case of this sort, considerable danger of overlooking the zinc. It is a significant fact that Fresenius uses hydrogen sulphide water in order to test for the zinc in the alkaline solution ("Anleitung z. Qualit. Chem. Analyse," 1874, 291). He is also careful to state that an excess of the reagent is to be avoided. However, in describing the special reactions of zinc he states that hydrogen sulphide precipitates from alkaline solutions all the zinc in the form of the hydrated sulphide (*loc. cit.*, p. 137). Nothing is said about an excess of the reagent, although he does mention the fact that ammonium chloride greatly promotes the separation of the precipitate.

In the following experiments I used a sodium hydroxide solution of zinc oxide containing 8 grms. of the oxide in a litre :—

1. Ten cc. of the solution were diluted to 150 cc. and treated with a rapid current of hydrogen sulphide. The zinc sulphide was precipitated almost immediately, but at the end of fifteen minutes it had passed into solution.

2. To 10 cc. of the solution, made faintly acid with hydrochloric acid, a few drops of a concentrated solution of manganous sulphate were added and the metals precipitated as sulphides with yellow ammonium sulphide. After filtering, dissolving the precipitate in a small amount of very dilute hydrochloric acid, and separating the manganese with excess of sodium hydroxide, the alkaline filtrate was diluted to about 150 cc. and treated with a rapid current of hydrogen sulphide. In fifteen minutes the zinc sulphide had dissolved and the solution was clear.

3. The experiment was repeated with a solution containing the same amount of zinc oxide along with considerable amounts of manganese, cobalt, and nickel. The alkaline solution of the zinc oxide, however, behaved toward the sulphuretted hydrogen gas exactly as it did in 1 and 2.

On standing, all three solutions became turbid, owing to a gradual separation of the zinc sulphide.—*Journal of the American Chemical Society*, xxx., No. 3.

Preparation of Argon from the Air by means of Calcium Carbide.—Franz Fischer and Oskar Ringe.—In this paper the authors describe in detail their new method of preparing argon from the air, which gives good yields of the gas at a comparatively low cost. The oxygen and nitrogen are absorbed by means of a finely powdered mixture of 90 per cent calcium carbide and 10 per cent calcium chloride, the absorption being carried out at 800° in an iron vessel specially constructed for the purpose. An apparatus for insuring thorough circulation of the air has been devised, and by means of it 11 litres of argon can be obtained by the aid of 7 kilogrms. of carbide in two days. The density of the gas was determined and found to be 19·94 (O = 16).—*Berechte*, xli., No. 10.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

Part III.—Analysis of the Aluminium and Iron Groups, including Beryllium, Uranium, Vanadium, Titanium, Zirconium, and Thallium.

By ARTHUR A. NOYES, WILLIAM C. BRAY, and ELLWOOD B. SPEAR.

(Continued from p. 33).

Tabular Outline.

In the accompanying tables the enclosure of a symbol in brackets shows that the element may divide itself between the residue and the solution in the operation immediately preceding.

Procedure and Notes.

Procedure 51.—Boil the filtrate from the H_2S precipitate (P. 21) till the H_2S is expelled. (For this and similar references to former procedures, see the previous article, *Journ. Am. Chem. Soc.*, xxix., 137). Transfer it to a flask, add NH_4OH (0·96) until the mixture after shaking smells of it, and then 2 to 4 cc. more. Note whether there is a precipitate. Add ammonium monosulphide slowly (or if nickel is likely to be present pass in H_2S), until, after shaking, the vapours in the flask blacken a piece of filter-paper moistened with lead acetate solution. To coagulate the precipitate shake the mixture, or heat it nearly to boiling. Filter, and wash the precipitate, first with water containing about 1 per cent of the $(NH_4)_2S$ reagent, and then with a little pure water. If the filtration is slow, keep the funnel covered with a watch-glass so as to prevent oxidation. To the filtrate add a few drops $(NH_4)_2S$, boil the mixture for a few seconds, or longer if it is dark coloured (till it becomes colourless or light yellow); filter if there is a precipitate, uniting it with the preceding one. (Precipitate, P. 52; filtrate, P. 71, or first by *P. 51*a*, if vanadium is to be tested for).

Notes.

1. The H_2S is boiled out, and the effect of the addition of NH_4OH alone is noted because it often gives a useful indication as to what elements are present. To save time the expulsion of the H_2S may be omitted when this indication is considered unimportant. Ammonium monosulphide is used, rather than polysulphide, in order to prevent as far as possible the dissolving of NiS, and in order not to introduce sulphur into the precipitate, or polysulphide into the filtrate; for this gives to the filtrate a deep yellow colour, and causes in the subsequent analysis separation of sulphur on standing or on heating. Excess of the monosulphide is avoided for the same reasons, since it rapidly oxidises in the air to polysulphide. By passing H_2S into the ammoniacal solution instead of adding $(NH_4)_2S$, the dissolving of NiS is entirely prevented; therefore, though the operation takes a little longer, the use of H_2S is to be preferred when nickel is likely to be present. The mixture is shaken in order to coagulate the precipitate and make it filter more readily. Heating also promotes the coagulation of the precipitate, and it is recommended when the precipitate does not coagulate and settle quickly on shaking. The filtrate is boiled for a few moments to ensure the complete precipitation of $Cr(OH)_3$, or longer to ensure that of NiS, whose presence is indicated by a brown or nearly black colour of the filtrate. Finally it is directed to wash with water containing a little $(NH_4)_2S$, and to keep the filter covered, in order to avoid the oxidation of the sulphides by the air, by which soluble sulphates may be formed.

2. Under the conditions of the procedure, which provides for a small excess of NH_4OH in the presence of NH_4Cl, aluminium, chromium, iron, titanium, zirconium, and beryllium are completely precipitated as hydroxides and uranium as ammonium diuranate, $(NH_4)_2U_2O_7$. All of these precipitates are white except those of chromium, uranium, and iron; $Cr(OH)_3$ is greyish green, and $(NH_4)_2U_2O_7$ is yellow. The colour of the precipitated hydroxide of iron varies with the state of oxidation of the iron, pure ferrous salts yielding a white precipitate, and ferric salts a reddish brown one, while mixtures of them yield green or black precipitates. In the alkaline mixtures the precipitate is rapidly oxidised by the oxygen of the air, and undergoes corresponding changes in colour. Manganous salts are also oxidised rapidly, with the result that brown $Mn(OH)_3$ separates. Under the conditions of the procedure zinc and nickel, when present alone, are completely dissolved; the same is true of cobalt except when it is present in large quantity, but zinc is precipitated when chromium is also present. The ammoniacal solution of nickel is blue and that of cobalt of a reddish colour, which darkens rapidly on exposure to the air owing to oxidation. If a smaller excess of NH_4OH is used than is directed, some zinc hydroxide, as well as cobalt hydroxide, may remain undissolved when large amounts of these elements are present, but this has no effect on the subsequent analysis. If, however, a much larger excess of NH_4OH is employed, a few mgrms. of aluminium and chromium may be dissolved, the latter giving a pink coloured solution.

3. The presence of a considerable quantity of NH_4Cl, such as is formed by the neutralisation of the acid already in the solution, serves to prevent the precipitation of $Mg(OH)_2$, and of $Mn(OH)_2$, and also to lessen the amount of $Al(OH)_3$ dissolved by the NH_4OH.

4. The influence of an excess of the NH_4OH and of the presence of NH_4Cl on the solubilities of the various hydroxides is explained by the mass action-law and ionic theory as follows:—In order that any hydroxide, say, of the type MO_2H_2, may be precipitated, it is necessary that the product $C_M.C^2_{OH}$ of the concentrations of the ions M++ and OH− in the solution in question attain the value known as the solubility-product. This varies, of course, with the nature of the hydroxide, but for all the elements of the iron group and also for magnesium it has so small a value that, even in a solution containing in 50 cc. only 1 mgrm. of the element and a slight excess of NH_4OH, the product $C_MC^2_{OH}$ exceeds it, and precipitation results. When, however, much NH_4Cl is also present, this greatly reduces, in virtue of the common ion effect, the ionisation of the NH_4OH and therefore the OH− concentration in the solution, so that now for certain elements the product $C_MC^2_{OH}$ does not reach the solubility value, even when C_M is moderately large (say, 500 mgrms. in 50 cc.). This is true of magnesium and manganese; but in the cases of aluminium, chromium, and ferric iron the solubility of the hydroxides in water is so slight that even in NH_4Cl solution the solubility is not appreciable.

If these were the only effects involved, the greater the excess of NH_4OH added, the less would be the solubility of any hydroxide, but other influences come into play with certain of the elements. These influences are of two kinds. The first of these is shown by zinc, nickel, and cobalt. In the case of these elements, just as with silver and copper, the excess of ammonia combines with the simple cation M++ forming complex cations of the types $M(NH_3)_2$++ and $M(NH_3)_4$++, thereby removing the simple cation from the solution and making it necessary for more of the hydroxide to dissolve, in order to bring back the value of $C_MC^2_{OH}$ to that o the solubility product. In such a case, the presence of NH_4Cl increases the solubility still further, since it greatly decreases C_{OH} and slightly increases C_{NH_4OH} and C_{NH_3}, owing to the common ion effect on the ionisation of the NH_4OH. Chromium also forms similar ammonia complexes, but in much smaller proportion.

The second effect is exhibited in the case of AlO_3H_3. This hydroxide is a so-called amphoteric substance; *i.e.*, is one which behaves both as a base and as an acid in

* From the *Journal of the American Chemical Society*, xxx., No. 4.

TABLE VII.

ANALYSIS OF THE ALUMINIUM AND IRON GROUPS FOR COMMON ELEMENTS.

To the filtrate from the H_2S precipitate add NH_4OH and $(NH_4)_2S$ (P. 51).

Precipitate: $Al(OH)_3$, $Cr(OH)_3$, ZnS, MnS, FeS, Fe_2S_3, NiS, CoS.—Dissolve in HCl or HCl+HNO_3, evaporate, add NaOH, Na_2O_2, and Na_2CO_3 (P. 52).

Filtrate: Alkaline earth and alkaline elements.

Filtrate: $NaAlO_2$, Na_2CrO_4, Na_2ZnO_2. — Acidify with HNO_3, add NH_4OH (P. 53).

Precipitate: $MnO(OH)_2$, $Fe(OH)_3$, $Co(OH)_3$, $Ni(OH)_2$, $Ni(OH)_3$, $[ZnO_2H_2]$.—Dissolve in HCl, evaporate, heat with HNO_3 and $KClO_3$ (P. 61).

Precipitate: $Al(OH)_3$. — Dissolve in HNO_3, add $Co(NO_3)_2$, evaporate, ignite (P. 54).

Blue Residue: $Al_2O_3.xCoO$.

Filtrate.—Add $HC_2H_3O_2$ and $BaCl_2$ (P. 55).

Precipitate: $BaCrO_4$. — Dissolve in dilute HNO_3, add ether and H_2O_2 (P. 56).

Blue Coloration of Ether Layer: H_3CrO_7.

Filtrate: Salt of Zn. — Pass in H_2S (P. 57).

White Precipitate: ZnS. — Dissolve in HNO_3, add $Co(NO_3)_2$, ignite (P. 57).

Green Residue: $ZnO.xCoO$.

Precipitate: MnO_2. Boil with HNO_3 and PbO_2 (P. 62).

Violet Colour: $HMnO_4$.

Solution.—Add NH_4OH (P. 64). (*a*).

Precipitate: $Fe(OH)_3$. Dissolve in HCl, add KSCN.

Red Solution: $Fe(SCN)_3$.

Filtrate: $Co(NH_3)x(NO_3)_2$, $Ni(NH_3)_4(NO_3)_2$, $Zn(NH_3)_4(NO_3)_2$.—Pass in H_2S (P. 66).

Precipitate: ZnS, CoS, NiS.—Treat with cold dilute HCl (P. 67).

Solution: $ZnCl_2$, $[CoCl_2]$, $[NiCl_2]$.—Add NaOH and Na_2O_2 (P. 67).

Residue: NiS, CoS.

Solution: Na_2ZnO_2. Add $HC_2H_3O_2$ and H_2S (P. 57).

Precipitate: $Co(OH)_3$, $Ni(OH)_{2-3}$.

Dissolve, evaporate, add NaOH.

White Precipitate: ZnS.

To one half add KNO_2 and $HC_2H_3O_2$ (P. 69).

To other half add KCN, digest, add NaBrO (P. 70).

Yellow Precipitate: $K_3Co(NO_2)_6$.

Black Precipitate: $Ni(OH)_3$.

(*a*) Test for phosphate at this point (P. 63); if present, follow Table IX.

TABLE VIII.—ANALYSIS OF THE ALUMINIUM GROUP FOR COMMON AND RARE ELEMENTS.

Filtrate from Na_2O_2 *Treatment*: Na_2CrO_4, sodium peruranate, Na_3VO_4, Na_2ZnO_2, $NaAlO_2$, Na_2BeO_2.—Add HNO_3, dilute, add $NaHCO_3$, heat in a closed bottle (*P. 58*a*).

Filtrate: Salts of chromic, uranic, and vanadic acids.—Add HNO_3 and $Pb(NO_3)_2$ (*P. 58*b*).

Yellow Precipitate: $PbCrO_4$.

Filtrate: $UO_2(NO_3)_2$, H_3VO_4, $[Pb(NO_3)_2]$.—Pass in H_2S.

Precipitate: PbS.—Reject.

Filtrate.—Add bromine, neutralise, add $HC_2H_3O_2$ and Na_2HPO_4 (*P. 58*c*).

Precipitate: $UO_2NH_4PO_4$. Dissolve in HCl, evaporate, add NaCl and $K_4Fe(CN)_6$ (*P. 58*d*).

Brown Precipitate: $(UO_2)_2Fe(CN)_6$.

Filtrate: H_3VO_4. Add NH_4OH, saturate with H_2S (*P. 58*e*).

Red Solution: Sulphovanadate.—Acidify (P. 58*e*).

Black Precipitate: V_2S_{4-5}.

Precipitate: $ZnCO_3$, $Al(OH)_3$, basic $BeCO_3$.—Dissolve in HCl, add NH_4OH (*P. 58*f*).

Filtrate: $Zn(NH_3)_4Cl_2$. Add $HC_2H_3O_2$, pass in H_2S (P. 57).

White Precipitate: ZnS.

Precipitate: $Al(OH)_3$, $Be(OH)_2$.—Dissolve in HCl, add ether, saturate with HCl gas (*P. 58*g*).

White Precipitate: $AlCl_3,6H_2O$.

Filtrate.—Evaporate, add 10 per cent $NaHCO_3$ solution, boil, pass in H_2S (*P. 58*h*).

Filtrate.—Acidify, boil, add NH_4OH.

Precipitate: $Al(OH)_3$, Fe_2S_3. Reject.

White Precipitate: $Be(OH)_2$.(*a*).

(*a*) Filter, and test the precipitate for uranium (*P. 58*h*).

TABLE IX.—ANALYSIS OF THE IRON GROUP FOR THE RARE ELEMENTS AND FOR THE COMMON ELEMENTS IN THE PRESENCE OF PHOSPHATE.

Precipitate from Na_2O_2 *Treatment*: $MnO(OH)_2$, $Fe(OH)_3$, $TlOH)_3$, $ZrO(OH)_2$, $TiO(OH)_2$, $Co(OH)_3$, $Ni(OH)_2$, $Ni(OH)_3$, $[Zn(OH)_2]$; $CaCO_3$, $SrCO_3$, $BaCO_3$, $MgCO_3$; and phosphates of these elements.—Dissolve in HCl, evaporate, heat with HNO_3 and $KClO_3$ (P. 61).

Brown Precipitate: MnO_2.

Solution.—Test a portion for iron; to the remainder add NH_4OH till nearly alkaline, then $NH_4C_2H_3O_2$ and $FeCl_3$, dilute, and boil (P. 65). (*a*).

Precipitate: Basic acetates, hydroxides, and phosphates of Fe, Tl, Zr, Ti.—Dissolve in HCl (1·12), shake with ether (*P. 65*a*).

Ether Layer: $FeCl_3$, $TlCl_3$.—Evaporate, dissolve in dilute H_2SO_4, add KI and Na_2SO_3 (*P. 65*d*).

Solution: $FeSO_4$.

Yellow Precipitate: TlI.

Water Layer: $TiCl_4$, $ZrCl_4$.—Add H_2SO_4, evaporate, add H_2O_2 and Na_2HPO_4 (*P. 65*b*).

White Precipitate: $Zr(OH)PO_4$.

Orange-yellow Filtrate: TiO_3.—Add Na_2SO_3 (*P. 65*c*).

White Precipitate: $Ti(OH)PO_4$.

Solution: Salts of Co, Ni, Zn, Ca, Sr, Ba, Mg. Add NH_4OH, pass in H_2S (P. 66).

Precipitate: NiS, CoS, ZnS. (See Table VII.).

Filtrate: Salts of Ca, Sr, Ba, Mg.

(*a*) Test for phosphate at this (Point. 63); if found absent, make the solution alkaline with NH_4OH (omitting the addition of ammonium acetate and $FeCl_3$), and filter.

consequence of its being appreciably ionised both into $3(OH^-)+Al^{+++}$ and into $H^+ + AlO_3H_2^-$ (or AlO_2^- and H_2O). With the H arising from the latter form of ionisation, the OH^- coming from the excess of NH_4OH combines to form H_2O, thus causing more AlO_3H_3 to dissolve until the value of $C_{AlO_2}.C_H$ again attains that of the solubility-product. Since $C_{AlO_2}.C_H$ = const. in any solution saturated with AlO_3H_3, and since the equilibrium equations $C_H.C_{OH} = K_W$ and $C_{NH_4}C_{OH} = K_3C_{NH_4OH}$ must be satisfied, it follows from combination of these equations that C_{AlO_2}/C_{OH} = const., and that C_{Al_2O} = const. $\times$ C_{NH_4OH}/C_{NH_4}. The first equation shows that the quantity of aluminium dissolved is proportional to the concentration of hydroxide-ion in the solution, and that therefore it would be much greater in a solution of a largely ionised base like NaOH than in that of a slightly ionised base like NH_4OH. The second equation shows that the solubility in solutions containing NH_4OH and NH_4Cl (or other ammonium salt) is proportional to the ratio of the concentration of the base to that of the salt; so that the presence of ammonium salts tends to neutralise the solvent action of an excess of the hydroxide. All these conclusions are in accordance with the facts. BeO_2H_2 behaves in the same way as AlO_3H_3, forming the cation Be^{++} and the anion $BeO_2^=$ or $HBeO_2^-$.

5. It follows from the statements in the preceding notes that if the NH_4OH produces no precipitate it proves the absence of as much as 1 mgrm. of aluminium, iron, beryllium, uranium, titanium, and zirconium, also of chromium, if the mixture is heated to boiling after the addition of NH_4OH. Care must be taken not to overlook a small precipitate which might otherwise escape detection on account of its transparency. The mixture should therefore be well shaken, and allowed to stand two or three minutes in order that the precipitate may collect in flocks. This treatment also oxidises the iron when present in small quantity, and thus enables it to be more readily detected; for its precipitation in the ferric state is more complete.

6. When phosphate is present, magnesium, calcium, strontium, barium, and manganese may be partially or even completely precipitated by NH_4OH. It is therefore necessary, when phosphate is present to provide for the detection of the alkaline earth elements in the analysis of this precipitate. The normal phosphates and the monohydrogen phosphates of these elements are difficultly soluble in water, but dissolve readily in acids, owing to the formation in solution of the much more soluble dihydrogen phosphates or of free phosphoric acid; for example, according to the equations:—

$$(Ca^{++})_3(PO_4^{\equiv})_2 + 4H^+ + Cl^- = 2Ca^{++} + (Cl^-)_2 + Ca^{++}(H_2PO_4^-)_2,$$

$$Ca^{++}(H_2PO_4^-)_2 + 2H^+ + Cl^- = Ca^{++} + (Cl^-)_2 + H_3PO_4.$$

Upon the addition of sodium or ammonium hydroxide to such a solution the hydrogen ion in equilibrium with the $H_2PO_4^-$ and H_3PO_4 is removed, and these dissociate into $HPO_4^=$ and $PO_4^{\equiv}$, thus causing precipitation of the corresponding salts. When other elements, like iron, forming more insoluble phosphates are also present, it is evident that they will combine with the phosphate radical, thus leaving the alkaline earth elements in solution. On the other hand, when a soluble carbonate, or a large excess of a strong base, is also present, the alkaline earth phosphates will be partially converted into carbonates or hydroxides, leaving phosphates in solution.

7. The presence of any other acid radical which forms with the alkaline earth elements salts soluble in dilute acids but insoluble in ammonia may also cause their precipitation at this point. Such radicles are fluoride, borate, oxalate, and hypovanadate. The fluoride will ordinarily have been removed in the evaporation with acids in the preparation of the solution. The borates of the alkaline earth elements, though somewhat difficultly soluble, are not sufficiently so to cause them to be precipitated, except when present in very large quantity. Oxalate and hypovanadate, even if present, do not make any change necessary in the usual process of analysis; for, in the course of it, vanadate and much of the oxalate are separated from the alkaline earths in P. 52, and the remainder of the oxalate is destroyed in P. 61.

*8. Vanadium when present alone in moderate quantity may remain in solution, but when present in large quantity is partially precipitated by NH_4OH as a dark grey hydroxide, $VO(OH)_2$. This compound corresponds to the state of oxidation (oxide VO_2) to which vanadic acid (oxide V_2O_5) is partially or completely reduced by H_2S. It is an amphoteric substance which forms with acids soluble blue salts such as $VOCl_2$, vanadyl dichloride, and $VOSO_4$, vanadyl sulphate, and with bases hypovanadates such as $Na_2V_2O_5$ and $Na_2V_4O_7$. When other elements of this group are also present the vanadium may be completely precipitated with them, since their hypovanadates and vanadates are, in general, difficultly soluble substances.

*9. When a base is added to a uranyl salt (for example, UO_2Cl_2), uranyl hydroxide, $UO_2(OH)_2$, is first formed, but this is an amphoteric substance, and it is converted by the excess of base into salts of diuranic acid, $H_2U_2O_7$, of which even the alkali salts are insoluble.

10. $(NH_4)_2S$ precipitates ZnS, MnS, NiS, CoS, and Tl_2S, and converts $Fe(OH)_2$ into FeS, $Fe(OH)_3$ into Fe_2S_3, and $(NH_4)_2U_2O_7$ very slowly into UO_2S. The hydroxides of aluminium, chromium, titanium, zirconium, and beryllium are not affected by the $(NH_4)_2S$. Whether a hydroxide precipitate is converted into a sulphide precipitate or whether the reverse reaction takes place depends on the relative solubilities of the two compounds and on the relative concentrations of sulphide-ion and hydroxide-ion in the solution. Since, in the solution the concentration of the sulphide-ion greatly exceeds that of the hydroxide-ion, even difficultly soluble hydroxides would be converted into more soluble sulphides, provided that the difference in solubility were not too great. In the case of hydroxides, like $Al(OH)_3$, which are not so changed, their sulphides are so much more soluble that they do not form in aqueous sulphide solutions.

11. The sulphides of iron, nickel, and cobalt are black, Tl_2S and UO_2S are dark brown, ZnS is white, and MnS is flesh coloured, but turns brown on standing in the air owing to oxidation to hydrated Mn_2O_3.

12. When nickel is present alone, or in large proportion in the $(NH_4)_2S$ precipitate, several mgrms. of it usually pass into the filtrate, making it dark coloured, and some NiS also passes through the filter with the wash water. In this case it is useless to try to remove the NiS by filtering again, but it can be coagulated by boiling for several minutes. This behaviour of nickel, as stated above, can be avoided altogether by passing H_2S into the NH_4OH solution to precipitate the sulphide, instead of adding $(NH_4)_2S$. The formation of this brown solution depends upon the presence of ammonium polysulphide, for nickel may be completely precipitated by ammonium monosulphide in the absence of air. The nature of the brown solution is not known.

(To be continued).

Crystalline Compound of Magnesium Methyl Iodide with Amyl Ether.—Th. Zerewitinoff.—To prepare this crystalline compound magnesium ribbon, dry methyl iodide, dry amyl ether, and iodine crystals are allowed to act upon one another. When the action has ceased the mixture is heated with an upright condenser. To the saturated CH_3MgI solution thus prepared paraffin is added, and the crystals of $CH_3MgI(C_5H_{11})_2O$ separate after standing for some days.—*Berichte*, xli., No. 10.

NOTICES OF BOOKS.

The Scientific Foundations of Analytical Chemistry. By Wilhelm Ostwald. Translated by George M'Gowan. Third English Edition. London: Macmillan and Co., Ltd. 1908.

The third English edition of this work has been prepared from the fourth German edition, which appeared in 1904. Prof. Ostwald has himself revised the proof-sheets, and a few minor alterations and additions have been made. The excellent philosophical treatment of elementary analytical chemistry given in the book entirely does away with both the spirit and the letter of the now happily obsolete mechanical methods of identifying and estimating the commoner ions, and a perfectly new character is given to practical work. The general principles of physical and chemical methods of separating different substances are treated in the first part, and the applications of them to special cases are discussed in the second, in which the metals are classed together in the usual analytical groups. An appendix describes some simple experiments, which can easily be performed, to illustrate the general principles which underlie analytical chemistry.

A Treatise on Qualitative Analysis and Practical Chemistry. By Frank Clowes, D.Sc. (Lond.), F.I.C. Eighth Edition. London: J. and A. Churchill. 1908.

It is perhaps unnecessary to call attention to the special features of a work which has reached its eighth edition, and which is as widely known as this for its admirably clear and concise directions for experimental work, both preparations and analysis. The book contains material for fairly advanced work, and the requirements of technical students as regards pure analysis have been taken into account, although no technical analyses are described. The section on the preparation and properties of gases has been revised, and in addition the detection of organic substances is treated rather more fully in this than in the previous editions.

Kelly's Directory of Chemists and Druggists. London: Kelly's Directories, Ltd. 1908.

This Directory contains lists of pharmaceutical, manufacturing, and analytical chemists, druggists, &c., alphabetically arranged according to the counties in which they reside, and also classified lists of trades and professions connected with chemistry and pharmacy both in London and the suburbs and in the counties. The names and addresses of veterinary surgeons are included, and the most important hospitals and dispensaries are also given. The book is well arranged and indexed, and special care has been taken to make it accurate and trustworthy in every respect.

Urbanora, the World's Educator. London: The Charles Urban Trading Co., Ltd. 1908.

The use of the bioscope as an educational instrument opens up vast possibilities, both in elementary and advanced instruction, provided that the films are really good for their purposes and are not selected merely for spectacular effect. The Urbanora Company has engaged experts to obtain moving pictures of subjects of interest in Nature study, geography, history, surgery, &c., and although it is impossible to express an opinion upon the value of the films from a printed list, the photographs appear to have been chosen carefully, and the pictures should fulfil their special mission of exciting the interest of the student. In geography and history they aid the imagination to form clear conceptions of unfamiliar places and occurrences; in natural science they provide unique opportunities of making observations, especially of animal life; and in surgery they enable operations to be followed in every detail by large numbers of students simultaneously, and materially assist the lecturer in making his subject clear.

Research Work on Indigo. By W. Popplewell Bloxam, B.Sc. (Lond.), F.C.S., F.I.C. Published by Order of His Majesty's Secretary of State for India in Council. 1908.

This book contains reprints of papers published in various scientific journals by the workers attached to the University of Leeds, who have been engaged during the years 1905 to 1907 in investigating the chemistry of indigo. The chief outcome of their experiments is the perfecting of the tetrasulphonate process of analysing indigo, and the reports on the process are here given in full together with the discussions which took place at the meetings before which the papers were read; these discussions are an interesting part of the volume, and often throw light upon difficulties or disputed points. In the summary of the work which has been done the author is able to make the gratifying announcement that he and his collaborators have been able to perform practically all the experimental work originally planned, and proposals are now made which, if followed, should help the indigo grower to recover to some extent from the effects of the competition of the synthetic substance. Definite suggestions as to details of the manufacture, and more especially of the analysis of the leaf and finished product, are made, and thus the future of the industry is practically left in the hands of the planter and of those whose duty it is to provide funds to endow further research, of which there is urgent need.

The San Francisco Earthquake and Fire of April 18, 1906. Reports by Grove Karl Gilbert, Richard Lewis Humphrey, John Stephen Sewell, and Frank Soulé. With a Preface by Joseph Austin Holmes. Washington: Government Printing Office. 1907.

The reports of the experts who inquired into the effects of the San Francisco earthquake and fire of 1906 are contained in this book. Although the three engineers acted perfectly independently, there is a remarkable unanimity about the conclusions they have drawn with regard to the structure and materials of buildings which are most likely to withstand the effects of seismic disturbances, and these conclusions should be carefully studied by civil engineers. The general results of the investigations are summarised, and every effort is made to emphasise the lessons which are to be learnt from both the earthquake and the fire which followed it. Many instructive illustrations reproduced from the original photographs taken by the investigators show very clearly what type of structure was most liable to destruction, and the effects of the earthquake on the surface of the land are illustrated. In addition plans show the direction of the fault, the formation of which was responsible for the disturbance, although the earthquake, as a natural phenomenon from a purely scientific point of view, is studied in brief outline only, as a fuller account is given of it elsewhere by the Californian commission appointed for the purpose.

Kolloidchemie und Photographie. ("Colloid Chemistry and Photography"). By Dr. Lüppo-Cramer. Dresden: Theodor Steinkopff. 1908.

This monograph contains a short introduction to the chemistry of colloids, in which the many isolated facts which have been observed are brought together, those which are of special importance from the point of view of photography being enlarged upon. The applications of colloid chemistry to photographic problems are next con-

sidered, and here the attempt is made to further the introduction of a more scientific spirit into photographic practice. The chemistry of colloids is put before photographers in such a way that its special interest for them is plainly visible, and at the same time the attention of chemists who are engaged upon the investigation of the colloidal state is called to the problems in photography which are waiting for solution. These are so numerous and of such fundamental importance, both in practice and theoretically, that their study cannot fail to provide work of great interest and results of permanent value. The other branches of physical chemistry have hitherto been more thoroughly investigated than photo-chemistry, but deficiencies in this respect are now rapidly being made up, and books such as this are valuable reading for students who are ready to undertake research and who want some aid in selecting a profitable subject for investigation.

Kolloides Silber und die Photohaloide. ("Colloid Silver and the Photo-haloids"). By CAREY LEA. Translated into German by Dr. LÜPPO-CRAMER. Dresden: Theodor Steinkopff. 1908.

THE discoveries of Carey Lea in the chemistry of photography were so valuable that they may almost be said to have opened up a new region in scientific photography, and this translation of his works will be welcomed by German chemists. The most important papers, which appeared in the *British Journal of Photography*, the *Photographic News*, and the *American Journal of Science*, are translated in full, and notes are added by the translator, giving some account of more recent work, and emphasising the special importance of Carey Lea's researches on the allotropic modifications, or, as we should call them now, the colloidal forms of silver, and upon the photo-salts regarded as adsorption compounds of the silver haloids with silver. A short biography of the author and appreciation of the value of his contributions to the chemistry of photography is added.

Beiträge zur Allgemeinen Kolloidchemie. ("Contributions to the General Chemistry of Colloids"). By Dr. B. SZILARD. Dresden: Theodor Steinkopff. 1908.

IN this short monograph an attempt is made to lay the foundation of a comprehensive system by which all the phenomena of the colloidal state can be linked up, and the laws and principles regulating them formulated. Although the author has shown discretion in bringing together his material, the outcome of his work is on the whole disappointing. It may be summarised in a few words: he has established the existence of both organic and inorganic substances which possess the properties of albuminous bodies. These substances give rise to complexes by reactions which are neither chemical nor catalytic, but differ essentially from both classes of reactions. The value of the monograph lies in the stimulative effect the study of it may have upon chemists who are engaged in the investigation of the phenomena of colloidal chemistry, and who may find in it suggestions for fresh research in new directions.

Transparent Clear Crystalline Liquids.—D. Vorländer. — The author has prepared double-refracting, crystalline liquids which are as clear as water and transparent when spread on a glass plate; they are viscous, but do not form threads, and under the microscope they appear free from any turbidity or matter in suspension. The clear crystalline liquids can be made turbid by any process which destroys the uniform arrangement of the molecules, and the author explains at some length the theory of molecular form to account for the phenomena of crystalline liquids.—*Berichte*, xli., No. 10.

CORRESPONDENCE.

THE POTENTIAL ENERGY OF THE ELEMENTS.

To the Editor of the Chemical News.

SIR,—May I be allowed to point out to Mr. Daniel J. Rankin that, although, if correct, his values for the potential energy of the elements would be of very great importance, they are valueless until the method employed in calculating them is explained and shown to be valid, for the question of their correctness depends upon the validity of the method of calculation, and also, of course, upon the data employed. —I am, &c.,

H. STANLEY REDGROVE.

The Polytechnic, Regent Street, W.,
July 17, 1908.

THE THERMO-CHEMICAL RELATIONS OF CARBON, HYDROGEN, AND OXYGEN.

To the Editor of the Chemical News.

DEAR SIR,—In the CHEMICAL NEWS of Jan. 26th, 1906 (vol. xciii., p. 37), I drew attention to values of thermo-chemical equivalence for carbon, hydrogen, and oxygen, giving approximate agreement with some organic compounds, when applied to the heat of formation of these compounds as compared with those obtained by experiment.

I find that similar results are obtained by comparing these thermo-chemical data in the case of the compounds cited below:—

	Experiment. Cals.	Calculated. Cals.
Tri-methyl methane	42·450	42·180
Tetra-methyl-methane. ..	47·850	48·990
Di-isopropyl	61·080	55·800

—I am, &c.,

J. C. THOMLINSON.

6, Villa View, Low Fell, Gateshead-on-Tyne,
July 13, 1908.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. cxlvi., No. 24, June 15, 1908.

Solubility of Silver Iodide in Ammonia. — H. Baubigny.—By the method of crystallisation the author has found that the solubility of this salt in ammonia is much less than has hitherto been believed. At 16° the solubility in ammonia of density 0·926 is roughly of the order of 1/6000.

Ammoniacal Arsenic Chloride.—MM. Besson and Rosset.—When dry ammonia gas acts on arsenic trichloride at −20°, a yellow solid is formed, with composition corresponding exactly to the formula $AsCl_3.4NH_3$, It sublimes *in vacuo* at 200°, the sublimate being a substance of formula $2AsCl_3.7NH_3$. The compound $AsCl_3.4NH_3$ dissolves in liquid ammonia, but the evaporation of the ammonia does not leave behind the original substance, and hence the ammonia does not behave like a simple solvent, but like a reagent.

Colloidal Barium Sulphate.—A. Recoura.—If barium sulphate is formed by double decomposition in glycerin, water can be added to dilute the glycerin without causing

the precipitation of the sulphate. If the barium sulphate is obtained by neutralising a solution of sulphuric acid with barium ethylate, the colloidal substance can be obtained free from any electrolyte. The stability of a colloidal solution of barium sulphate is much increased by the addition of barium chloride or nitrate, and many electrolytes have no action upon the colloidal solution when barium salts are present, although they coagulate the pure solution.

Constitution of Tetramethyldiaminobenzhydryl Methylene Compounds.—R. Fosse.—If Weil's conclusion that tetramethyldiaminobenzhydrol is a ketone is correct the author's hydryl methylene compounds must result from the replacement of one atom of oxygen by a divalent residue, $=C<^{X}_{Y}$. The only compound the hydrol could yield with a mono-substituted methylene would be formed by the condensation of one molecule of ketene with two molecules of alkyl methylene. This conclusion is not confirmed by experiment. The hydrol unites with one molecule of methyl methylacetylacetate and methyl methylacetylacetone, yielding new hydrylmonoalkyl methylene compounds. The author has studied the properties of some of these new compounds and of their derivatives.

Action of Alkalis on Mono and Dimethyl Arsenic Acids and their Iodine Substitution Products.—M. Auger.—When caustic soda acts on sodium methylarsenate the latter is decomposed quantitatively at 250—280°, according to the equation :—

$$CH_3.AsO_3Na_2 + NaOH = CH_4 + AsO_4Na_3.$$

The same reaction occurs when sodium cacodylate is used. Triiodoacetic acid is very readily decomposed by alkalis into iodoform and alkaline carbonate, $CI_3CO_2Na + NaOH = CI_3H + CO_3Na_2$. Similarly, sodium diiodomethylarsenate and tetraiodocacodylate are split up by aqueous alkalis, giving methylene iodide :—

$$CHI_2AsO_3Na_2 + NaOH = CH_2I_2 + AsO_4Na_3,$$
$$(CHI_2)_2AsO_3Na + 2NaOH = 2CH_2I_2 + AsO_4Na_3.$$

Thus the atom of arsenic is detached from the molecule more readily than the two atoms of iodine bound to the carbon. This explains the quantitative formation of methylene iodide when a boiling solution of trisodium arsenite acts on iodoform. The iodoform unites with the tribasic arsenite, giving diiodomethylarsenate, $CHI_3 + AsO_3Na_3 = CHI_2AsO_3Na_2 + NaI$. Then this is decomposed by the alkali giving methylene iodide.

Lactone of Dioxy-3.4-butyric Acid.—P. Carré.—To prepare this lactone the monochlorhydrin of glycerin is diluted with water and potassium cyanide is added. When all action has ceased, concentrated sulphuric acid is added, and the whole is allowed to stand over-night. The chlorides of ammonium and potassium formed are filtered off, the solution is evaporated to dryness, and the residue taken up with acetone. After the latter has been distilled off baryta is added, and the solution of barium dioxybutyrate is precipitated with alcohol. The dioxybutyric acid is obtained by decomposing with alcohol. It loses water at 100°, and at a higher temperature two fractions can be distilled off; one is the lactone of oxy-4-crotonic acid and the other the lactone of dioxy-3.4-butyric acid. The latter is a colourless liquid, which can be distilled *in vacuo* without undergoing decomposition.

Double Phosphate of Magnesium and Monomethylamine.—Maurice François.—A double phosphate of magnesium and monomethylamine of formula $PO_4 \equiv^{Mg}_{NH_3.CH_3.6H_2O}$ is known. It has been obtained in the crystalline state by mixing solutions of magnesium sulphate and sodium phosphate with monomethylamine. The corresponding phosphates of di- and trimethylamine do not appear to exist. Quantin's method of separating mixtures of di- and trimethylamine and ammonia cannot be applied to the separation of ammonia and monomethylamine.

No. 25, June 22.

Heat of Neutralisation of Acetic and Benzoic Acids, by Aniline in a Benzene Medium.—Léo Vignon and M. Evieux.—When the heats of neutralisation of acetic and benzoic acids by aniline in benzene solution are determined, it is found that no reaction occurs between the acids and base, and no salt is formed, thought salt is formed when the two substances are brought together either in the dry state or in aqueous solution. Apparently the salts first formed are destroyed by being dissolved in benzene.

New Method of Separating Silica and Tungstic Anhyride.—Ed. Defacqz.—The mixture of silica and tungstic anhydride is heated to a red heat in a current of hydrogen. Between 600° and 900° silica is not reduced by hydrogen, nor has chlorine any action upon it, while at the same temperature hydrogen reduces tungstic anhydride to lower oxides, or even metal, and chlorine readily yields hexachloride or oxychloride. When the action is over the substance is heated in a glass tube to a red heat in a current of dry chlorine, and the volatile products are condensed. All the tungstic anhydride then volatilises either as hexachloride or oxytetrachloride. This is dissolved in aqueous ammonia, and the tungsten is determined in the solution in the usual way. The residue of silica is weighed after the chlorine has been expelled by heating in air or hydrogen. This method of separation can be applied to any mixture of compounds containing oxygen, if one of the compounds can be reduced by hydrogen, and the resulting substance yields a volatile chloride.

Constitution of Derivatives of Diphenylmethane and Preparation of Ortho-di-amino Compounds of the same Series.—H. Duval.—The constitution of monoacetyldiphenylmethane is easily established, for when oxidised by chromic acid in acetic solution it yields benzophenone-*p*-carbonic acid. To prove the formula of dinitrodiphenylmethane dicarbonic acid, *o-o*-dinitro-*p-p*-diaminodiphenylmethane is diazotised and treated with cuprous cyanide. The *p-p*-dinitrile is thus obtained, and on saponification it gives the *o-o*-dinitrodiphenylmethane *p-p*-dicarbonic acid identical with the product obtained by directly nitrating diphenylmethane *p-p*-dicarbonic acid. The oxidation of ethyl *o-o*-dinitrodiphenylmethane *p-p*-dicarbonate by chromic acid in acetic solution leads to the formation of ethyl *o-o*-dinitrobenzophenone *p-p*-dicarbonate, the same substance as that obtained by oxidising dinitro-*p-p*-diacetyldiphenylmethane by excess of hypobromite, and treating with alcohol and hydrochloric acid. When nitric acid acts on *p-p*-diacetyldiphenylmethane in sulphuric acid solution *o-o*-dinitrodiphenylmethane *p-p*-dicarbonic acid is obtained.

β-Alcohol α-α-Dialcoholated Ketones. Transposition by Dehydration.—E. E. Blaise and I. Herman.—The ketone, $CH_2OH—C(CH_3)_2—CO—C_2H_5$, is transposed by alkalis, giving the unsaturated ketone methovinylisopropyl ketone, $\begin{matrix}CH_3\\CH_2\end{matrix}\equiv C—CO—CH(CH_3)_2$. This might be explained in two ways :—Either a migration of the alcohol group occurs, followed by dehydration, or else dehydration is first effected, and then the methyl group migrates. Since the dehydration of oxydivalylethyl ketone does not lead to the formation of methovinylisopropyl ketone, it follows that the former explanation is correct, transposition occurring first and then dehydration.

Berichte der Deutschen Chemischen Gesellschaft, Vol. xli., No. 10, 1908.

Liquid Crystals.—Th. Rotarski.—The author gives an account of the properties and preparation of some liquid crystalline compounds which have not been described before. These include dianisyltetylene, $(CH_3O.C_6H_4.CH:CH)_2$, methoxycinnamic acid, methylamidobenzalphenylhydrazine, diethylbenzidine, bisdiphenylmethylol-biphenyl,

$[(C_6H_5)_2C(OH)C_6H_4—]_2$, and methoxy-cinnamic aldazine. The first of these is particularly interesting, for it shows that in methoxycinnamic acid the anisotropic liquid phase is not due to carboxyl or hydroxyl groups, but to the group $CH_3O.C_6H_4.CH:CH$, which is common to both substances.

Stereoisomerism in Compounds with Asymmetric Carbon and Pentavalent Asymmetric Nitrogen.—M. Scholtz.—The addition of halogen alkyl to alkylated *d*-coniin gives two different addition products with different physical properties. This phenomenon is due to the asymmetry of the pentavalent nitrogen atom. The same stereoisomerism can be observed in conhydrin and *α*-methyl-*α'*-phenyl piperidine. On the other hand, the addition of halogen alkyl to optically active alkaloids (except alkylated coniin and conhydrin) gives only one ammonium compound. It is found that the existence of two stable forms in *α*-substituted piperidine derivatives is conditioned by the volume occupied by the *α*-substituent which gives stability to the atomic groups attached to the neighbouring nitrogen atom. *α*-Picoline, however, behaves differently from piperidine derivatives with larger *α*-substituents, for it gives only one addition product with alkyl halogen. This appears to be because the methyl group, whether it is directly united with the asymmetric nitrogen or is the *α*-substituent in the pyridine ring, has not sufficient influence to give rise to two stable isomers.

Reduction of Alkyl Nitrates to Nitrites by reducing Salts in Alkaline Solution.—A. Gutmann.—The action of alkalis or arsenites upon alkyl thiosulphuric acid salts yields sulphite and thioethylhydroperoxide :—

$$SO_3Na.SC_2H_5 + NaOH = SO_3Na_2 + C_2H_5.SOH.$$

$$SO_3Na.SC_2H_5 + As(ONa)_3 + NaOH = SO_3Na_2 + AsO(ONa)_3 + C_2H_5.SK.$$

This behaviour is due to the per-acid character of thiosulphuric acid. As nitric acid has a similar character it might be expected that the nitric acid esters would behave in the same way as the thiosulphuric acid salts towards alkaline reducing agents, such as arsenites, cyanides, and sulphides. This is found to be the case with the ethyl and isoamyl esters of nitric acid, which behave precisely as predicted, according to the equations—

$$NO_2.OC_2H_5 + NaOH = NO_2.Na + C_2H_5.OOH.$$

$$C_2H_5.OOH + As(ONa)_3 = C_2H_5OH + AsO(ONa)_3.$$

Preparation of Boron Nitride and of Calcium Boride.—Alfred Stock and Walter Holle.—Boron bromide, which can be obtained comparatively easily in the pure state, reacts with ammonia, giving ammonium bromide and borimide, $BBr_3 + 6NH_3 = B(NH_2)_3 + 3NH_4Br$. Borimide is converted on heating into boron nitride. It is best to allow the bromide to drop into excess of liquid ammonia, and special precautions have to be taken in order that the tube through which the bromide is introduced does not get stopped up when it reaches the atmosphere of ammonia. It was found that the boron obtained from magnesium and boron trioxide is not pure enough to be used for making the boron bromide for this synthesis, and the authors endeavoured to prepare the element by reducing boron trioxide with calcium. At a dark red heat, however, this reaction does not lead to the formation of boron, but of almost pure calcium boride.

Double Dissociation of Quaternary Ammonium Compounds and Synthesis of Iodoaceto-nitrile.—J. v. Braun.—Iodoaceto-nitrile in the cold yields the direct addition product with dimethylaniline, and this product splits up quantitatively on warming as shown by the equation—

$$2C_6H_5.N(CH_3)_2(CH_2CN).I = C_6H_5.N(CH_3)_3.I + I.CH_2.CN + C_6H_5.N(CH_3).CH_2.CN.$$

Evidently the addition product undergoes double decomposition into four substances—$C_6H_5.N(CH_2)_2 + I.CH_2.CN$, $C_6H_5N(CH_3)CH_2CN + ICH_3$, the first and fourth of which then unite. Iodoacetonitrile can conveniently be prepared from methylcyanomethyl aniline by warming it with methyl iodide, the equation—

$$C_6H_5.N(CH_3)_2 + I.CH_2.CN \rightleftharpoons [C_6H_4.N(CH_3)_2(CH_2.CN.I] \rightleftharpoons C_6H_5.N(CH_3).CH_2.CN + ICH_3$$

occurring towards the left when excess of methyl iodide is used. These decompositions with bromo and iodoacetonitrile are the first known instances of the decomposition of an ammonium halogen compound yielding a halogen alkyl. In all cases in which tertiary aromatic bases react easily with iodoacetonitrile the reaction can be used to attach the cyanated methyl group to the tertiary nitrogen.

Characterisation of Primary, Secondary, and Tertiary Bases with 1 . 5-Dibrompentane.—J. v. Braun.—When 1 . 5-dibrompentane acts on primary amines in which there is an open chain, a hydrated carbon ring, a heterocyclic ring, or a benzene ring not substituted in the *o*-position, tertiary piperidines are obtained—

$$(CH_2)_5Br_2 + 3H_2NR = (CH_2)_5{>}NR + 2NH_2R.BrH.$$

These piperidines have basic properties and can be obtained in a pure state by distillation. If the benzene ring contains one or two substituents in the ortho position to the amido group, pentamethylenediamine derivatives, $R.NH.(CH_2)_5.NH.R$, are formed. Secondary amines of the fatty series, piperidine, &c., give with dibrompentane only quaternary piperidinium compounds :—

$$(CH_2)_5Br_2 + 2HNR_2 = (CH_2)_5{>}NR_2Br + R_2NH.HBr.$$

Secondary aromatic bases yield the same substance as the principal product of the reactions, besides small quantities of tertiary pentamethylene diamine bases, $R_2N.(CH_2)_5.NR_2$. Tertiary bases give only diammonium bromides—

$$(CH_2)_5Br_2 + 2NR_3 = Br(R_3)N.(CH_2)_5.N(R_3)Br.$$

MISCELLANEOUS.

Institute of Chemistry.—*Pass List, July Examinations*, 1908.—Of twenty-four candidates who presented themselves for the Intermediate Examination in London and Glasgow, the following fifteen passed :—H. L. Allen ; B. S. Evans, B.Sc. (Lond.) ; C. E. C. Ferrey ; H. A. Goldsbrough ; L. Goodban ; T. R. Greenough, B.A. (Cantab.) ; D. Henville ; G. Hogan ; A. P. Imrie ; G. E. Johnson, B.Sc. (Lond.) ; Osman Jones ; H. T. Reeve ; E. H. Shepherd, B.Sc. (Lond.) ; R. W. Warrick ; and J. Young. Twenty candidates presented themselves for the Final Examination in the Branch of Mineral Chemistry, held in London and Glasgow, and fourteen passed :—J. Boyd ; J. Brebner, M.A., B.Sc. (Aberdeen) ; R. Bruce ; G. S. Butler, B.A. (Oxon.) ; A. M. Cameron, B.Sc. (Edin.) ; W. Cameron ; G. A. M. Cunningham ; M. C. Fletcher ; G. A. Freak, B.Sc. (Lond.) ; J. V. J. Hayman, A.C.G.I. ; A. Hepburn ; J. W. H. Pattison ; A. S. Petrie ; and Miss M. M. J. Sutherland. In the Branch of Metallurgical Chemistry, of two examined in London, one passed :—R. T. Rolfe. One candidate was examined in the Branch of Physical Chemistry, but did not satisfy the Board. Of nine candidates who presented themselves in the Branch of Organic Chemistry in London and Glasgow, the following four passed :—N. C. Akers ; J. Kenyon, B.Sc. (Lond.) ; H. R. Norton, B.Sc. (Lond.) ; and W. F. Russell. The Examination in the Chemistry of Food and Drugs, and of Water, was held in London, and of six who presented themselves for the Associateship in this Branch, five passed : —H. A. Caulkin, B.Sc. (Lond.) ; H. Heap, M.Sc. (Manc.) ; A. S. Joy, Assoc. R.C.Sc. (Lond.) ; C. J. H. Stock, B.Sc. (Dun.) ; and C. H. Warner. Three candidates were examined in this Branch for the Fellowship, and two passed :—K. S. Caldwell, B.Sc. (Wales), Ph. D. (Leipzig) ; and A. R. Tankard.

THE CHEMICAL NEWS.

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NOTES ON LABORATORY APPARATUS.

By W. HEBER GREEN, D.Sc., University of Melbourne.

I. On the Determination of Density by means of the Ordinary Pear-shaped Specific Gravity Bottle.

Several authorities have objected to the use of this apparatus; thus, Ostwald, in "Physico-chemical Measurements," p. 90, says:—"An unpractical form of the pycnometer is in very general use. This is a small bottle with a ground-in and perforated stopper, its contents when the stopper is inserted forming the *supposed constant volume* in question. As the conical angle of the stopper must be small in order to get it to fit tight, a slight elastic deformation of the neck causes a considerable displacement of the stopper in the direction of its axis, which creates a by no means negligible source of error not easily to be avoided.

"To attain a more rapid equilibrium of temperature it is better to make the bottle cylindrical than spherical as usually happens."

Against this statement must be put the fact that in a number of determinations of the density of water by means of a pear-shaped specific gravity bottle of 25 cc. capacity, it was found that the maximum error liable to occur was about 0·00002, equal to 0·5 mgrm., and that even this was almost entirely due to variations in the buoyancy of the atmosphere.

But in order to obtain this accuracy certain precautions were found to be necessary. The ordinary specific gravity bottle can only be used for temperatures above that of the surrounding atmosphere; in order to take an observation it was filled with the solution, and immersed to the neck in a thermostat whose temperature did not vary by more than 0·04°, and it was found that expansion of the solution through the perforated stopper was complete in from ten to fifteen minutes. The bottle was then removed from the bath, wiped dry, placed in the balance case to cool for fifteen minutes, and weighed at once to prevent loss by evaporation.

In accurate work the buoyancy of air is an essential factor.

If W = apparent weight of water required to fill the bottle;
M = apparent weight of solution required to fill the bottle; and
d = true density; then—

$$= \frac{M}{W}\left(1 + \frac{0{\cdot}0012}{d} - 0{\cdot}0012\right).$$

Or the following amounts should be subtracted from the observed apparent densities:—

Approximate density of solution .	1·1	1·2	1·33
Correction for buoyancy of air . .	0·0001	0·0002	0·0003

The above formula is only approximate, and entirely disregards variations of atmospheric density, which often amount to over 5 per cent of the total, and are sufficient to nullify the correction for all but the most concentrated solutions usually worked with.

When required, the most practical and accurate method of correcting for the buoyancy of air would be to use as a counterpoise a similar but sealed glass vessel of the same external volume as the specific gravity bottle, and weighted with shot or mercury until slightly heavier than the latter when full of water. This should replace the all but useless brass counterpoise now so often supplied by the manufacturer.

Perhaps the most serious fault to be found with the ordinary laboratory instrument is that the stopper is only roughly ground in, for it is obvious that the more carefully it is fitted the less will the capacity of the bottle be affected by its rotation.

In two bottles that were employed by the writer the stoppers were carefully re-ground with fine and flour emery, and at the same time the capacities were adjusted so that at the temperatnre of experiment the apparent weight in grms. of the water contents was exactly twenty-five times the true density of water.

In the course of time the repeated wear on the ground surfaces of the stopper and neck slightly diminishes the capacity of the pycnometer.

If the same bottle be used at different temperatures then allowance must be made for the expansion of the glass.

An obvious refinement would be to make the bottle of Jena glass, or preferably of fused silica.

II. A Simple but Extremely Sensitive Form of Thermo Regulator.

In a piece of physico-chemical work carried out in this laboratory various patterns of thermo regulator were used

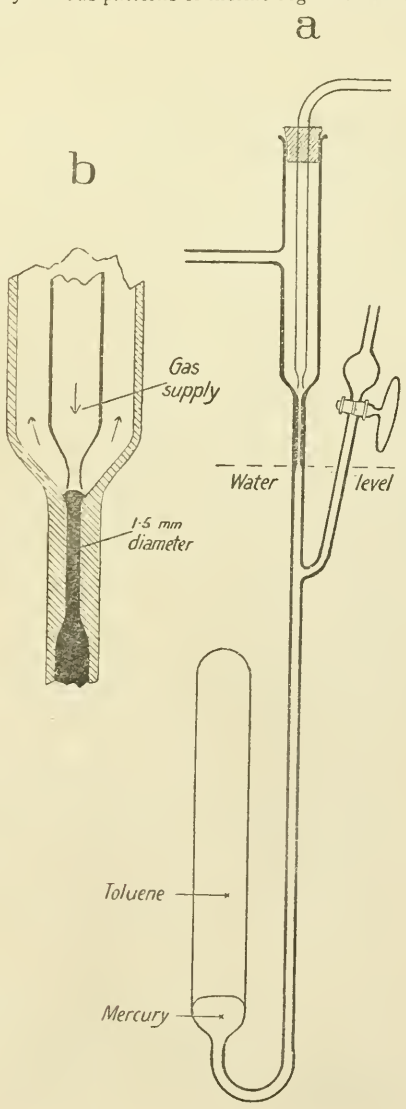

Fig. 1.

but finally a form was adopted, the most important novelty of which is that the orifice of the gas inlet tube is slightly opened out (see Fig. 1) instead of being left square, or cut off at an angle, or even constricted, as is often recommended.

In this form, as soon as the drop of mercury reaches and closes the funnel-shaped opening of the tube, its capillarity tends to force it down again and admit the gas supply; in the older forms the mercury will not enter and close the tube until an appreciable head of liquid has accumulated, and the required temperature exceeded, and will only be forced out again by the gas pressure with a rush when the temperature has fallen too low, and so an oscillatory instead of a steady temperature is apt to be maintained.

With this improved thermostat having a bulb of about 20 cc. filled with toluene as figured, the temperature was found to remain constant to at least within 0·01 for days and even weeks at a time, as long as the water in the bath was efficiently stirred, and this was provided for by means of a small propeller driven at high speed so as to cause a definite current up one side of the bath and down the other. A change from one temperature to another is readily effected by opening the tap of the thermostat, and, when the bath is at the desired temperature, adjusting the level of the mercury by suction applied through a rubber tube.

III. A Sensitive Temperature-compensated Barometer.

One drawback to the ordinary mercury barometer is that readings cannot be obtained accurate to 0·01 inch unless special precautions are observed and temperature corrections taken into account.

Water or glycerin barometers being about thirty feet high are sensitive, but unwieldy. Huyghens long ago suggested a combination of the mercury and glycerin barometers. In his form a narrow tube about a foot long was sealed on to the upper end of the wide tube containing the mercury; the glycerin was placed on top of the mercury and its upper free surface being in the small tube gave a sensitive indication of small movements of the mercury. By choosing tubes whose areas are as 1 : 30 a magnification of 6·28 could be obtained, but the temperature correction becomes increasingly important. With water instead of glycerin on top of the mercury, the changes of vapour pressure produce an error in the opposite direction, but of much greater magnitude.

After several experiments it was found that the vapour pressure of a paraffin oil (boiling-point about 230° C.), obtained by fractional distillation of kerosene, varied with the temperature at such a rate as almost exactly to neutralise the effects of the accompanying expansion of the mercury for the particular dimensions of tubes that were used.

A syphon barometer made in this way rises or falls one inch for a rise or fall of an eighth of an inch in the pressure of the air, and clearly indicates the momentary fluctuations of pressure inside the laboratory on a windy day.

The disadvantages of the instrument are:—

1. The difficulty of filling the tube and getting the liquid and top of the tube free from permanent gases. It is necessary to fill it from the upper end and advisable to leave a mercury trap into which any remaining gas can be forced after the apparatus is completed.
2. It is cumbersome, being over four feet long and not very portable.
3. It must be graduated by an arbitrary scale after comparison with a standard instrument.

Its advantages are:—

1. Great sensitiveness. A glance from a distance of several yards enables an observer to tell with certainty if the air pressure has altered by as little as one-hundredth of an inch during the progress of an experiment on, say, the boiling-point of a liquid or solution.

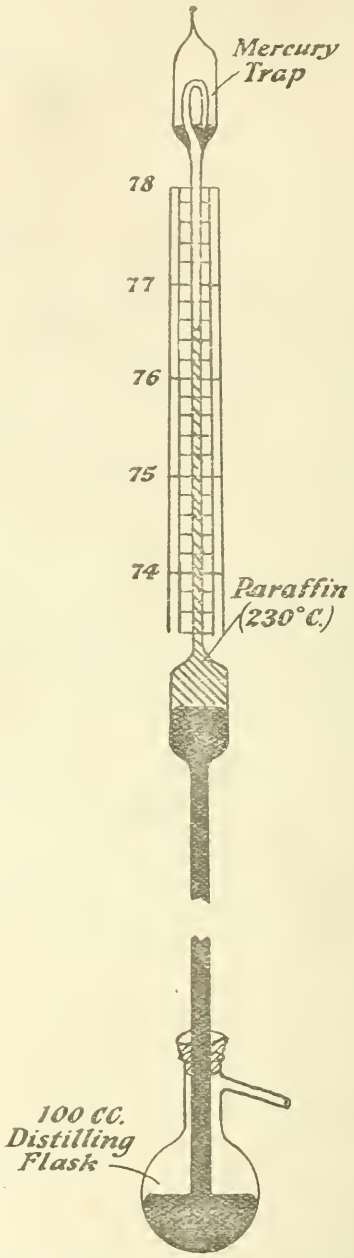

Fig. 2.—Sensitive Barometer.

2. The mercury surface in contact with the paraffin is always clean, and does not stick to the glass, and consequently responds instantly to minute changes of atmospheric pressure without tapping.
3. It is *automatically* compensated for changes of temperature.

About two years ago an English firm of scientific instrument makers advertised a sensitive temperature compensated barometer of a somewhat similar appearance, but gave no details of its construction or the principles on which it depended.

THE ESTIMATION OF GRAPHITE.

By FRANK BROWNE, F.I.C., Government Analyst, Hongkong.

When graphite is heated at a bright red in an uncovered dish with ferric oxide several changes may be noted. The carbon entirely disappears, and the ferric oxide, though apparently unchanged at the surface, is darker in colour towards the bottom of the dish, owing to the formation of magnetic oxide. In order to see if the error due to this loss of oxygen could not be avoided, the action of heat and of various chemical reagents on ferric oxide has been studied, until finally it was found that heat alone could be so applied as to solve the difficulty.

If ferric oxide after being heated at a pale red in a *covered* crucible be then heated in the *uncovered* crucible at the same temperature, it slowly gains in weight, until after an hour's heating, provided always a fairly even temperature is maintained, the weight remains constant. If the heat be decreased from a pale to a dull red, then the oxide again increases in weight. Slight variations in temperature make practically no difference to the oxide, but it is essential in using the process hereinafter described that as even a temperature as possible should be maintained, and with a little practice this can be done without difficulty, and judging only by the eye. Based on the foregoing observations a process for the estimation of graphite has been devised. The ferric oxide to be used should be heated in a covered crucible at a pale red for two or three hours. The resulting oxide should be a slightly coherent magnetic powder, nearly black in colour. It will be found to be but very slightly hygroscopic. About 5 grms. of this oxide are taken, placed in a small uncovered shallow dish or wide mouth crucible, and heated at a temperature not exceeding a pale red for an hour, with occasional stirring, then weigh. Add about 0·5 of the graphite, stir together, and heat as before for one to two hours, stirring once or twice, and weigh. The carbon will be burnt off, and the oxide remains at the end in the same condition as at the commencement. When one estimation is finished another weight of graphite may be put into the same used oxide. A sample of graphite containing 9·15 per cent of mineral matter by potash fusion gave 8·98 and 8·96 per cent by this iron oxide method. Graphite freed from mineral matter showed by this process 99·73 per cent of carbon.

The mineral matter of coal may be determined in the same way, but the amount found will be about 0·5 per cent higher than as determined in the ordinary manner. This is what might be expected, as when coal is burnt to an ash the constituents are likely to react together, thus giving a figure somewhat lower than the true amount. Individual determinations, whether of graphite or coal, by this process will be found to agree closely; thus, using quantities from 0·5 to 1 grm. of coal, 9·21, 9·24, 9·34, and 9·35 per cent of mineral matter were indicated.

THE IODOMETRIC DETERMINATION OF ARSENIC AND ANTIMONY ASSOCIATED WITH COPPER.

By F. H. HEATH.

It has been said that the iodometric process for the determination of copper can be used without error in the presence of arsenic and antimony provided that the latter elements are in the higher condition of oxidation. A. H. Low makes this statement and gives careful directions for the complete oxidation of the arsenic and antimony (*Journ. Am. Chem. Soc.*, xxiv., p. 1083). There appears, however, to be no record of any attempt to determine arsenic and antimony iodometrically after the separation of copper from a mixture containing the three elements.

It has been thought worth the while, therefore, to attempt the determination of arsenic and antimony in the filtrate from cuprous iodide after titration of the free iodine by means of sodium thiosulphate, and filtration. To this end the attempt has been made to reduce the arsenic and antimony by boiling with potassium iodide and sulphuric acid according to the method of Gooch and Gruener (*Am. Journ. Sci.*, Sept., 1891, xlii.) and determining these elements by reoxidation with a standard solution of iodine. The reactions involved in these processes may be expressed by the general symbols $M_2O_5+4HI = M_2O_3+H_2O+2I_2$, and $M_2O_3+4I+2K_2O = M_2O_5+4KI$.

The trials of the method were made with tartar emetic and potassium arseniate. The tartar emetic was dissolved in water and the antimony oxidised to the higher condition by means of standard iodine solution in presence of sodium or potassium bicarbonate. The amount of iodine required was taken as a measure of the amount of antimony used. The solution of antimony thus obtained, or the solution of arsenic taken in the higher condition of oxidation, was acidified and a known volume of a standard solution of copper nitrate was added. The copper was determined iodometrically with precautions previously recommended by Gooch and Heath (*Am. Journ. Sci.*, 1907, xxiv., 65).

A special precaution to be observed is the choice of the acid used during the determination of copper. Mineral acids must not be present on account of their tendency to bring about reduction of the arsenic and antimony by action of the excess of potassium iodide used in throwing out the copper. Such action causes high results on copper and low results on arsenic and antimony. A mixture of acetic acid and potassium iodide reduces the higher salts slowly. Tartaric acid is somewhat irregular in action and tends to cause an interfering precipitation of acid potassium tartrate. The action of citric acid is more favourable. The amount of iodine set free by the combined action of citric acid and potassium iodide upon an arsenic compound in the higher condition of oxidation is appreciable if the solution is allowed to stand, while in the case of an antimonic salt the action is not nearly so rapid.

A few determinations were carried out to test the action of citric acid quantitatively. Portions of tartar emetic were oxidised to the higher condition by iodine in presence of sodium bicarbonate, the solution was then acidified with citric acid, weighed amounts of citric acid and potassium iodide were added, and the solution was allowed to stand for a definite time to find whether there was any reduction. When the solution was acidified, after the oxidation with iodine solution, a little iodine was set free, and this was bleached with a drop of sodium thiosulphate before continuing the experiment. For the test with arsenic a standardised solution of potassium arseniate was used. The results of these experiments are shown in Table I.

From these results it appears that in the iodometric determination of copper associated with arsenic there must be no delay in titrating the iodine even when the free acid is citric acid; otherwise, some reduction of the arsenic acid and liberation of iodine may take place, thus affecting the result of the copper determination. Antimonic acid is not reduced appreciably, in a reasonable time, under similar conditions.

In the course of preliminary work the fact developed that tetrathionic acid, which results from titration of free iodine by sodium thiosulphate in the copper determination, makes trouble in the subsequent operation. For, when the solution is boiled, after addition of sulphuric acid, the tetrathionic acid decomposes to give hydrogen sulphide and free sulphur, and sulphides of antimony and arsenic may be precipitated. Various means were tried to oxidise the tetrathionic acid and its decomposition products before reducing the arsenic and antimony. Solid iodine and potassium nitrite were tried for this purpose, but not very successfully. Bromine water and, better, liquid bromine were used with success.

It was found that if liquid bromine was added to the cold solution in sufficient quantity to decompose all the excess of potassium iodide present, and the solution then boiled, there was very little subsequent trouble on account

Table I.—*Effects of Citric Acid and Potassium Iodide in Reducing Arsenic and Antimonic Salts.*

Sb taken.	As taken as KH_2AsO_4.	Citric acid used.	KI used.	Vol. of solution.	Time of standing.	I found.
Grms.	Grm.	Grm.	Grm.	Cc.	Minutes.	Grm.
0·1209	—	3	4	60	10	No colour with starch.
0·0797	—	3	2	50	20	
0·1057	—	3	3	60	20	
					> 60	Trace.
—	0·1238	2	3	50	10	0·0009
—	0·1238	2	4	60	10	0·0012
—	0·1238	3	3	50	10	0·0019
—	0·1238	3	5	75	10	0·0017
0·1211	0·1238	3	5	100	10	0·0010
0·1211	0·1238	3	5	100	10	0·0017

Table II.—*Copper and Arsenic.*

KI used.	Vol at end of precipitation.	Cu taken.	Cu found.	Error in Cu.	Liquid bromine used.	KI used.	As taken.	As found.	Error in As.
Grms.	Cc.	Grm.	Grm.	Grm.	Cc.	Grms.	Grm.	Grm.	Grm.
3	50	0·0700	0·0700	—	1·0	2	0·1238	0·1231	−0·0007
3	50	0·0700	0·0693	−0·0007	1·0	2	—	0·1231	−0·0007
3	50	0·0875	0·0869	−0·0006	1·0	2	—	0·1239	+0·0001
4	50	0·0700	0·0698	−0·0002	0·6 0·4	1	—	0·1235	−0·0003
4	45	0·0700	0·0703	+0·0003	1·0	2	—	0·1247	+0·0009
4	50	0·0700	0·0700	—	1·0	2	—	0·1235	−0·0003
5	70	0·1400	0·1407	+0·0007	1·0 0·5	2	—	0·1233	+0·0005
5	50	0·0910	0·0907	−0·0003	1·0 0·5	2	—	0·1239	+0·0001
4	50	0·0700	0·0703	+0·0003	1·0	2	—	0·1237	−0·0001
4	50	0·0875	0·0879	+0·0004	1·0	2	—	0·1234	−0·0004
5	65	0·1400	0·1410	+0·0010	1·0	3	—	0·1239	+0·0001
3	30	0·0875	0·0860	−0·0015	0·8	2	0·0495	0·0493	−0·0002

Table III.—*Copper and Antimony.*

KI used.	Vol. at end of precipitation.	Cu taken.	Cu found.	Error in Cu.	Liquid bromine used.	KI used.	Sb taken.	Sb found.	Error in Sb.
Grms.	Cc.	Grm.	Grm.	Grm.	Cc.	Grms.	Grm.	Grm.	Grm.
4	85	0·0700	0·0703	+0·0003	1·0 0·5	2	0·1417	0·1421	+0·0004
4	80	0·0700	0·0701	+0·0001	1·0 0·5	2	0·1727	0·1725	−0·0002
4	80	0·0875	0·0869	−0·0006	1·0 0·5	2	0·1286	0·1289	+0·0003
5	80	0·0735	0·0739	+0·0004	1·0 0·5	2	0·1641	0·1645	+0·0004
5	90	0·1050	0·1050	—	1·0 0·5	2	0·1378	0·1372	−0·0006
4	75	0·0875	0·0874	−0·0001	1·0 0·5	2	0·1329	0·1326	−0·0003
6	115	0·0700	0·0707	+0·0007	1·3 0·5	2	0·2474	0·2477	+0·0003
8	120	0·1575	0·1571	−0·0004	1·5 0·5	2	0·1419	0·1413	−0·0006

of tetrathionic acid. To decompose the remainder of the potassium iodide used in the precipitation of the copper about one cubic centimetre of bromine was added. If, after boiling for a short time, the solution did not become clear, it was cooled, a little more bromine added, and the boiling repeated to ensure complete oxidation and to expel excess of bromine. It is well to concentrate the solution somewhat at this point so as to remove most of the bromine; otherwise, when potassium iodide is added to bring about reduction of the arsenic or antimonic salt, so much of it may be decomposed by the bromine that the reducing action may not be complete. Some free iodine remains in the solution after the reduction process, and there was found to be some difficulty in bleaching it with exactness in the hot solution. If the solution was cooled starch iudicator could be used. Accordingly in the cooled solution the free iodine, in presence of starch indicator, was bleached by adding an excess of dilute sulphurous acid. The solution was then diluted to 100 cc. or more and iodine solution added to a faint colour. This pale blue colour was then just bleached by careful addition of dilute sulphurous acid from a pipette. The solution was neutralised by use of sodium or potassium bicarbonate, and the arsenic or antimony determined by titration with standard iodine solution in the usual way. Following are tables showing results obtained by this method.

The procedure for the determination of copper and arsenic or of copper and antimony may be outlined as follows:—To the solution containing the copper and also the arsenic or antimony in the higher condition of oxidation, add 1 grm. to 2 grms. of citric acid. To precipitate amounts of copper not exceeding 0·3 grm. in a volume of

TABLE IV.

Copper, Arsenic, and Antimony.

KI used. Grms.	Volume at end of precipitation. Cc.	Copper. Cu taken. Grm.	Cu found. Grm.	Error in Cu. Grm.	As taken as KH_2AsO_4. Grm.	I required by theory to oxidise As. Cc.	I used to oxidise Sb. Cc.	Sb taken as found by I used. Grm.	Br used. Cc.	KI used in reduction. Grm	I required by theory to oxidise As and Sb. Cc.	I used to oxidise As and Sb. Cc.	Error in terms of I.(*a*) Grm.
—	—	—	—	—	0·1238	32·54	17·87	0·1088	1·0	2	50·41	50·06	−0·0043
—	—	—	—	—	0·0495	13·01	13·46	0·0820	1·0	2	26·47	26·46	−0·0001
—	—	—	—	—	0·1238	32·54	15·40	0·0938	0·5	2	47·94	47·70	−0·0030
—	—	—	—	—	0·0990	27·21	18·12	0·1054	1·0	2	45·33	44·90	−0·0053
									1·0				
5	90	0·0700	0·0718	+0·0018	0·0495	13·01	17·15	0·1044	0·5	2	30·16	30·00	−0·0020
									1·0				
5	90	0·0700	0·0710	+0·0010	0·0990	27·21	21·86	0·1272	0·5	2	49·07	49·00	−0·0009
									1·5				
(*b*) 5	95	0·1222	0·1223	+0·0001	0·0990	27·21	29·68	0·1727	0·3	2	56·89	56·23	−0·0081
9	115	0·0875	0·0868	−0·0007	0·0990	27·21	20·20	0·1176	2·0	3	47·41	46·90	−0·0063
6	110	0·1050	0·1067	+0·0017	0·0990	27·21	15·55	0·0905	1·3	2	42·76	42·64	−0·0015
(*b*) 7	100	0·1613	0·1611	−0·0002	0·0990	27·21	18·92	0·1101	1·5	2	46·13	45·90	−0·0028

(*a*) Weight of iodine × 0·50 = error calculated entirely on Sb; weight of iodine × 0·30 = error calculated entirely on As.
(*b*) Separate portions of Cu were weighed out.

50 cc. add 3 grms. of potassium iodide; in a volume of 100 cc. add 5 grms. of potassium iodide. Titrate the free iodine with sodium thiosulphate solution. The reactions involved in the copper determination are $2CuSO_4 + 4KI \rightarrow 2K_2SO_4 + Cu_2I_2 + I_2$ and $2I + 2Na_2S_2O_3 = 2NaI = Na_2S_4O_6$. Filter off the cuprous iodide on asbestos. To the filtrate add 1 cc. of liquid bromine and boil the solution in an Erlenmeyer flask, using a trap to prevent loss by spattering. If, after boiling for a short time and allowing the large amount of free iodine to volatilise, the solution does not become clear, cool it, add a little more bromine (0·5 cc.) and boil again. When the solution has become clear, concentrate it somewhat (to about 60 cc.) to expel excess of bromine. Dilute to about 100 cc., add 2 grms. of potassium iodide, and boil to a volume of 50 cc. Cool the solution, bleach the free iodine by adding sulphurous acid, using starch as indicator. Dilute to 100 cc., add iodine solution to colour, and just bleach by careful addition of dilute sulphurous acid from a pipette. Neutralise the solution with sodium or potassium bicarbonate and titrate the arsenic or antimony with standard iodine solution in the usual way.

From the results obtained it seems possible by this method to separate and determine copper and arsenic, or copper and antimony, with errors of only a few tenths of a milligrm. It is also possible to determine the sum of arsenic and antimony present with a fair degree of accuracy, and to separate and determine copper when associated with both arsenic and antimony. In the latter case the sum of the arsenic and antimony may also be determined, but the values here obtained for copper tend to come a little too high and those for arsenic and antimony a little too low.

In conclusion, the author wishes to express his appreciation of the kind assistance and many suggestions given by Professor F. A. Gooch during the course of these investigations.—*American Journal of Science*, xxv., p. 513.

RESEARCHES ON THE DENSITY OF GASES.*

By PHILIPPE A. GUYE.

THE present article contains a *résumé* of the results obtained during the course of three years' work on the exact density of gases. The work has been carried on in collaboration with Messrs. Jaquerod, Pintza, Davila, Gazarian, and Baume, and until now has been the subject of only isolated publication (Jaquerod and Pintza, *Comptes Rendus*, 1904, cxxxix., 129—SO_2 and O_2; Guye and Pintza, *Comptes Rendus*, 1904, cxxxix., 679; 1905, cxli., 51—N_2O, CO_2, and NH_3; Guye and Davila, *Comptes Rendus*, 1905, cxli., 826—NO; Guye and Gazarian, *Comptes Rendus*, 1906, cxliii., 1233—HCl; Baume, unpublished, 1907—SO_2). These have contributed to the problem of the physico-chemical determination of exact molecular weights, with a view to checking up the atomic weights. This problem has become one of great importance, and has been taken up by Leduc (*Recherches sur les Gaz*, Paris, Gauthier-Villars, in part; *Ann. Chim. Phys.*, 1897); Lord Rayleigh (*Proc. Roy. Soc.*, 1888, xliii., 353—H_2 and O_2; 1892, l., 449—H_2 and O_2; 1893, liii., 134—O_2, H_2, N_2 atmo. air; 1894, lv., 340—N_2; 1896, lix., 198—Ar, He; 1897, lxii., 204—CO, CO_2, N_2O; 1904, lxxiv., 181—N_2O; *Phil. Trans. Roy. Soc.*, 1905, cciv., A, 351) Rayleigh and Ramsay (*Phil. Trans. Roy. Soc.*, 1895, clxxxvi., A, 187), Morley (*Zeit. Phys. Chem.*, xx., 1—O_2; xxii., 1896, xxii., 2—H_2), Gray (*Journ. Chem. Soc.*, 1905, lxxxvii., 1601—N_2, O_2, NO_2; *Proc. Chem. Soc.*, 1907—HCl), as well as Perman and Davies (*Proc. Roy. Soc.*, 1906, lxxviii., A, 28). Details of the methods and the method of cal-

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culating the results, will be given under the head of generalities; next a review of the results obtained at Geneva compared with those of other experimenters, and finally a summary of those values which appear to the author to be most reliable.

I. *Generalities.*

Methods.—Two general methods have been used in density determinations, that of the balloon and that of the volumeter.

The balloon method, the details for which have been worked out by Regnault (weighing the balloon empty and filled with gas, against a counterpoise of the same volume, reducing to weight *in vacuo*, &c.) has been used in recent work, taking into account the correction for the contraction of the empty balloon, and the correction for the compressibility of the gas (deviation from the law of Mariotte between the existing pressure and that of 760 mm. Hg). The recent work is also characterised by a gradual reduction of the capacity of the balloon. Morley worked with balloons of from 8 to 21 litres capacity. Rayleigh used one of about 1·8 litres capacity, Leduc one of about 2·3 litres. The work in this laboratory has led to a still further reduction of the capacity of the balloon, and two balloons, destined to act as checks upon each other, one 0·8 litre, the other about 0·4 litre in capacity, filled at 0°, and under the same pressure conditions have been used. (Experiments using still smaller balloons are being carried on at present).

Perman and Davies have used a balloon of 0·5 litre capacity, while Gray has reached the lowest unit, and in the determination of nitric oxide used one of about 0·267 litre. Contrary to what one might expect, *à priori*, the determinations with the small balloons are at least as concordant, among themselves, as those with balloons of larger volume. The experiments with the 2-litre balloons below, show, on the whole, a better agreement than those with balloons varying from 8 to 21 litres. This may be due either to the fact that the corrections for the original weights (for contraction, &c.) are smaller with the small balloons, or that the chances of accidental error, especially those due to the condition of the surface of the glass, are diminished.

The only objection which can be raised to the use of the small balloons is the possibility of the condensation of gas on the inner wall. If there were such condensation, the density of gases measured in small balloons should be greater than in the larger balloons, and this error should be especially great in the case of the hygroscopic gases, sulphur dioxide, ammonia, hydrochloric acid gas, &c.

The recent determinations show that while the capacity of the balloons varies to a great extent, the results obtained are very concordant, especially in the case of ammonia and sulphur dioxide.

By the volumeter method (capacity = about 1·8 litres) Perman and Davies found 0·77085 grm. for the weight of a litre of ammonia gas under standard conditions, while by the balloon method they obtained 0·77086 grm. for the same gas, using a balloon of 0·5 litre capacity. Guye and Pintza, using a volumeter of 3·5 litres capacity, found 0·7708. Thus there is no appreciable difference between the values obtained by the large and small balloons. Jaquerod and Pintza have obtained the value 2·9266 grms. for the weight of 1 litre of sulphur dioxide, using a volumeter of 3·5 litres capacity; Leduc, using a 2·3 litres balloon, found 2·9266; and Baume has recently repeated this determination, using two balloons of 0·53 litre and 0·32 litre capacity, respectively, on gas prepared under the same conditions as that used by Jaquerod and Pintza, and has found 2·9266 grms.

The only necessary precaution consists in rinsing the balloon, not only with air dried over phosphorus pentoxide, but also several times with the well-dried gas, the density of which is to be determined, taking care that between each rinsing operation the vacuum in the balloon is as perfect as possible, and that air does not enter the balloon between each determination.

It might nevertheless be assumed that there is a slight condensation of the gas on the inner wall of the glass, similar to the moisture adhering to glass. The author's experience (in collaboration with Gazarian) on the density of hydrochloric acid gas, which is extremely hygroscopic, does not justify this assumption. In fact, the balloons were at first rinsed only two or three times with dry hydrochloric acid gas. Under these conditions with a balloon of 0·385 litre capacity, the values for the density showed a regular decrease, and did not become constant until after the fourth determination. Using a larger balloon (0·818 litre capacity) this point was not reached after the seventh filling. These facts led to the conclusion that after twelve successive rinsings with the dry gas, each rinsing followed by a complete evacuation of the balloon, the condensation of the gas on the interior wall of the balloon is not sufficiently great to affect the results to an appreciable extent, provided, air has not entered the balloon during the process of rinsing. (In the case of non-hygroscopic gases 5 to 6 successive rinsings, each followed by complete evacuation, are sufficient). (If Bunsen's observations are correct, the moisture given off by the glass at high temperatures is not due to condensation on the surface, but to water incorporated chemically or physically in the mass of the glass. (See Note).

(Note.—If we admit that the condensation of the gas on the interior surface of the balloon is not generally appreciable, still we do not claim that it is absolutely nil. In order to determine the condensation most accurately, two or more balloons of very different capacities should be filled at the same time, under the same conditions of pressure, and with gas from the same source. The determinations of the densities of nitric oxide and sulphur dioxide, using two balloons filled simultaneously, furnish some preliminary information on this subject. The following averages have been found for the weight of a litre of these gases, determined simultaneously with two balloons:—

Weight of a Litre of NO (*G. and D.*).

No. of observation.	Capacity of balloon. Litre.	Weight of 1 litre. Grms.
7·	0·8	1·3401
7·	0·4	1·3403
5·	0·5	2·92666
4·	0·3	2·92659

It may be claimed that this condensation was not on the surface of the glass, but in the special grease used to insure a tight cock. It may be well to cite here the recent work of Swinton (Chemical News, 1907, xcv., 134), who has shown that the gases, hydrogen and helium, have no chemical action on the surface of glass, and that the surface condensation is of a purely mechanical nature. The recent observations of Travers (*Proc. Roy. Soc.*, 1906, lxxviii., A, 9) on the condensation of gases by solid bodies should not be overlooked, if the density of a gas is to be determined with an accurracy exceeding 1 part in 10,000).

The *volumeter method*, used as an exact method for the first time by Morley in the determination of the density of hydrogen has been used in two ways. According to the first method the gas is evolved from an apparatus which may be weighed, and constructed in such a fashion that the gas alone, in a state of perfect purity and dryness, escapes. The gas then passes through a tight-fitting joint into a system of one or more balloons of known capacity, maintained at 0°, and which have been evacuated by a mercury pump. The pressure is measured either with a special manometer or simply by connecting the apparatus with the tube of a barometer. Morley employed the latter method in his fourth series of measurements of hydrogen, and it has also been employed at Geneva. Knowing then the temperature and the pressure, the capacity of the balloons, and the loss of weight of the generating apparatus, the density may by calculated.

According to the second method the volumeter, previously evacuated, is filled with the pure gas. The process

of purifying may be more complete, as there is no limit to the weight of the apparatus used for that purpose. The volumeter being filled with the pure gas is held at 0°, and the exact pressure about (760 mm.) is read. Then the gas is absorbed in a suitable apparatus, previously evacuated and weighed, and connected to the volumeter by a tight-fitting joint.

The densities of hydrogen (Morley), oxygen, and sulphur dioxide (Jaquerod and Pintza) have been determined by the first method, by the second those of nitrous oxide, carbon dioxide, and ammonia (Guye and Pintza), and, more recently, ammonia (Perman and Davies).

The volumeter method used does not take into account the correction for the contraction of the balloons, but only that necessary for the reduction of the weights to weights *in vacuo* (for the evolution or absorption apparatus is weighed with a counterpoise of the same glass and the same volume), and finally the pressure coefficient of the gas in order to calculate the volume at a pressure of 760 mm.

Whichever method is employed (balloon or volumeter), the correction for the pressure coefficient of the gas is negligible, since the pressure differs from 760 mm. by only a few mm.

Choice of a Unit.—A common unit is indispensable. Leduc has reduced his values either to the density with regard to air, or to the weight of a litre of gas at Paris, or both. Morley expresses his results in weight per litre under standard conditions; that is, at 0° and 760 mm. pressure, at sea-level and latitude 45°. Rayleigh calculates his results either to density compared with air or compared with oxygen (taken equal to 32), or as the weight of 1 litre at London or at Paris. At Geneva the weight of the litre under standard conditions has been directly determined. Gray, as well as Perman and Davies, has likewise used this unit, which is the unit for all results which are given in the following pages.

D. Berthelot (*Comptes Rendus*, 1907, cxliv., 269) has recently calculated the greater number of measurements, comparing densities to that of oxygen. Instead of taking one value for oxygen, he adopts, in each case, the value obtained by each investigator for the density of this gas. This system presents several disadvantages:—First, in the case of those determinations made by investigators who have not determined the value for oxygen, the choice of such a value becomes somewhat arbitrary. Second, it might happen that the value for oxygen, even when determined by the investigator, was the most inaccurate of all his determinations; thus the accuracy of his other values would be diminished. This is, the case, for example, at Geneva, where the value for oxygen has been determined with less precision than for the other gases.

These disadvantages disappear when all results are calculated to the weight of 1 litre of the gas under standard conditions. All the investigators, with the exception of Leduc, have recorded the exact volume of the balloons employed. Leduc's values may be calculated, since he has determined the weight of a litre of air at Paris.

There is, finally, another reason for expressing the density by the weight per normal litre, and that is the fact that the volume of the balloon can be calibrated more accurately than the weight, of a gas for comparison, can be determined in the same balloon. Leduc reports that after an interval of two years the capacity of a balloon originally found to be 2·27636 litres, was 2·27630 litres, or the variation was 1 : 38,000. At Geneva an accuracy of 1 part in 30,000 to 35,000, between successive calibrations, has been easily realised. It is necessary to determine the capacity of the balloon for water at 0°, and under these conditions no correction for the expansion of the glass is required. (Difficulty was experienced in weighing the balloon filled with water at 0°, as the water expands when the balloon is placed on the balance. This has been overcome by attaching a bulb tube to the tubule of the balloon, by means of a ground joint or a rubber tubing, the whole apparatus having a counterpoise of the same glass and the same volume).

Choice of Final Values.—The following are some of the rules which have guided us in making a choice between the various values obtained for the density of each gas.

First, the nature of the method employed for the production and purification of the gas has been taken into consideration. This is, to our mind, the most important consideration in the density determinations. Those results showing concordance in the values obtained for the gas prepared in two or three different ways have therefore been given most weight.

A second consideration, equally important, is the concordance obtained by different investigators for the same gas. When the average values of two observers agree, while that of a third experimenter differs by a considerable amount, they have not been given equal weight, but the third value has been given less weight than the first two. Frequently, an experimenter has made a more or less accurate determination of the limit of error of his work. We have applied the correction in such a way as to bring the value nearer the mean of the other two observers. Similarly, when an error was discovered in the course of subsequent work, we have not taken into account that value known to be erroneous.

As will appear in the following discussion, while the preceding rules are suggested, an accurate choice is difficult to make. We would add that, in abandoning several of Leduc's values, giving preferences to others, generally more recent, in their stead, there has been no intention of diminishing the importance of Leduc's work. If the modern determinations have benefited by a more perfect technique, still we must recognise that to Leduc belongs the credit of having been the first to give a complete solution, theoretical and experimental, of the problem of the rigorous determination of the molecular weights of gases as a function of their densities.

(To be continued).

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

Part III.—Analysis of the Aluminium and Iron Groups, including Beryllium, Uranium, Vanadium, Titanium, Zirconium, and Thallium.

By ARTHUR A. NOYES, WILLIAM C. BRAY, and ELLWOOD B. SPEAR.

Continued from p. 44)

Procedure and Notes (continued).

Procedure 51*a*.—To the filtrate from the $(NH_4)_2S$ precipitate (P. 51) add 5 cc. NH_4OH (0·90), and completely saturate the solution with H_2S. (Pink or violet-red colour, presence of *vanadium*).

If no red colour results, boil the solution for several minutes in a casserole to expel most of the NH_4OH and $(NH_4)_2S$, filter off the sulphur, and treat the filtrate by P. 71.

If the solution assumed a pink or red colour, acidify it with HCl (1·12), heat it to boiling, and filter. Boil the filtrate in a casserole to expel H_2S, add 0·5 to 5 cc. 10 per cent $FeCl_3$ solution, and NH_4OH (0·96) until the mixture after shaking smells of it, and filter. (Filtrate, P. 71). Heat the HCl precipitate (with the filter if necessary) with 5 to 10 cc. HNO_3 (1·20) until the black precipitate is dissolved, and filter. (If the red coloration produced by H_2S was slight, evaporate the filtrate to about 2 cc.). Add to the solution a few drops of 3 per cent H_2O_2. (Orange-yellow or orange-red colour, presence of *vanadium*). Dissolve the NH_4OH precipitate by pouring a small portion of HNO_3 (1·20) repeatedly through the filter, and test for

* From the *Journal of the American Chemical Society*, xxx., No. 4.

vanadium with H_2O_2 in the same way, first adding a little water to the HNO_3 solution if it has a red colour owing to the presence of much ferric nitrate.

Notes.

1. An ammoniacal solution of a vanadate or hypovanadate quickly becomes yellowish red when H_2S is led into it, and this colour slowly deepens as more H_2S is absorbed, but the characteristic brilliant violet-red colour is obtained only when the solution is completely saturated with H_2S. The presence of ammonium salts tends to prevent the formation of this red compound, but their influence is overcome by the addition of a large excess of NH_4OH. These facts make it probable that this red compound is an ammonium sulphovanadate, from which the sulphur is readily split off as SH− ion, owing to hydrolysis. Under the conditions of procedure, 0·2 mgrm. V can be easily detected, the solution then having a pink colour.

2. Upon the addition of HCl the sulpho salt is immediately decomposed, with formation of a black precipitate of V_2S_4 or V_2S_5. This precipitation is far from complete under these conditions, only about half the vanadium being thrown down. More or less sulphur will also be precipitated, but the dark colour of the sulphide is apparent even when less than 0·5 mgrm. V is present. Acetic acid may be used instead of HCl, but the proportion of vanadium precipitated as sulphide is not much increased.

3. When a three- to fivefold excess of a ferric salt is present and NH_4OH is added, the remainder of the vanadium is precipitated (probably as hypovanadate) together with the $Fe(OH)_3$.

4. The confirmatory test for vanadium with H_2O_2 depends upon the formation of pervanadic acid, HVO_4. 0·1 to 0·2 mgrm. V may be detected in a volume of 5 cc., provided that this solution is strongly acid. A very large excess of H_2O_2 is to be avoided, for this decreases the intensity of the colour, and may even decolorise the solution completely, if very little acid is present, probably owing to the formation of a colourless compound of pervanadic acid with hydrogen peroxide.

5. Molybdenum, if not completely precipitated by H_2S in P. 21, and tungsten, if it passed into the original acid solution (owing to the presence of phosphate or arsenate) in P. 3, may also be present in the filtrate from the $(NH_4)_2S$ precipitate. Upon saturating with H_2S molybdenum also gives a deep red colour which would obscure the test for vanadium, and might be mistaken for it, but tungsten gives no colour. Upon acidification with HCl, tungsten divides between the precipitate and filtrate, but molybdenum is thrown down completely as black MoS_3. (If the cold solution is acidified with acetic acid, the sulphomolybdate remains undecomposed for some time, and the MoS_3 is not completely precipitated even on boiling). In the final confirmatory test with H_2O_2 tungsten gives no colour, and molybdenum, even when a large quantity is present, gives only a pure yellow colour, but not an orange or red one.

Procedure 52.—Transfer the $(NH_4)_2S$ precipitate (P. 51) with the filter if necessary to a casserole; add 5 to 20 cc. HCl (1·12), stir for a minute or two in the cold, and then boil the mixture for two or three minutes; if a black residue still remains, add a few drops HNO_3 (1·42), and boil again. Dilute with a little water, filter off the sulphur residue, and evaporate the filtrate to a small volume to remove the excess of acid.

*In order to detect rare earth elements, and to remove them if present, treat this solution by *P. 52*a*.

*If uranium and vanadium are to be tested for later by *P. 58*a—h*, evaporate twice with a little HNO_3 (1·42), to destroy HCl.

Dilute the solution to 10 or 20 cc., make alkaline with NaOH solution, avoiding a great excess; add 10 to 20 cc. more water if so large a precipitate separates that the mixture becomes almost gelatinous. Cool by placing the casserole in cold water, and add 0·5 to 3 grm. solid Na_2O_2, in small portions with constant stirring. Then add 5 cc. 10 per cent Na_2CO_3 solution; boil for two or three minutes to decompose the excess of Na_2O_2, cool, dilute with an equal volume of water, filter with the help of suction, and wash with hot water. (Precipitate, P. 61; filtrate, P. 53, or if uranium or vanadium is to be tested for, *P. 58*a*).

Notes.

1. All the hydroxides and all the sulphides, except NiS, CoS, usually dissolve readily in cold HCl. If therefore there is considerable black residue after adding the HCl, it shows the presence of nickel or cobalt (or possibly vanadium); a very small black residue may, however, be due to FeS enclosed within sulphur. The fact that there is no such dark coloured residue does not, however, prove that nickel and cobalt are absent, for a considerable quantity of them (even 5 mgrms.) may dissolve completely in the HCl when large quantities of other elements, especially iron, are also present.

2. The fact that NiS and CoS dissolve so much less readily in dilute acids than do the other sulphides of this group seems to be due not to a lesser solubility in water, but to an unusually slow rate of solution, for nickel and cobalt are not precipitated by H_2S, even from a much more weakly acid solution, and their sulphides obtained by precipitation with an alkaline sulphide continue to dissolve in dilute acids without reaching a limit determined by the concentration of the H_2S and the nickel-ion or cobalt-ion in the solution, as would be the case if the phenomena were that of the solubility of a difficultly soluble sulphide.

3. The $(NH_4)_2S$ precipitate is first treated with HCl, partly in order to furnish the indication just referred to of the presence of nickel or cobalt, but mainly because much more free sulphide and sulphate would be formed by oxidation if HNO_3 or *aqua regia* were used at the start. The presence of the sulphate in considerable quantity in the solution interferes with the subsequent test for chromate (with $Ba(NO_3)_2$ in P. 55 or with $Pb(NO_3)_2$ in *P. 58*b*). If NiS, CoS, or V_2S_5 is present in the residue, HNO_3 must, however, be subsequently added to ensure the solution of these sulphides. *The HCl is destroyed by evaporation with HNO_3, since chloride interferes with the test for chromate with $Pb(NO_3)_2$ in *P. 58*b*.

*4. If the $(NH_4)_2S$ precipitate be allowed to stand for a long time before treating it with acid, or if the mixture be heated for a long time after the precipitation, $TiO(OH)_2$ and $ZrO(OH)_2$ may remain in part undissolved even by the boiling concentrated acids, owing to the fact that the hydroxides at first precipitated become partially dehydrated, in which state they are very difficultly soluble. If this happens at this point or in dissolving hydroxide precipitates obtained later in the analysis, the residue may be dissolved in a little HF in a platinum dish, and the HF then expelled by evaporating two or three times with HNO_3 (or HCl) nearly to dryness.

5. By NaOH, iron, manganese, nickel, cobalt, *titanium, *zirconium, and *uranium are completely precipitated, and do not dissolve in moderate excess; while aluminium, chromium, zinc, *vanadium, and *beryllium remain in solution or dissolve when a sufficient excess is added, owing to the fact that their hydroxides are amphoteric substances (see P. 51, N. 3), and form with the NaOH soluble aluminate, $NaAlO_2$; chromite, $NaCrO_2$; zincate, Na_2ZnO_2; vanadate, Na_3VO_4; and beryllate, Na_2BeO_2. Thallium in the thallous state also remains in solution, since TlOH is a readily soluble substance. When zinc and chromium are simultaneously present, they are precipitated in the form of a double compound, $ZnCr_2O_4$. Chromium would also be completely precipitated, owing to hydrolysis and the formation of a less soluble solid hydroxide, if the NaOH solution were boiled before adding Na_2O_2. It will be observed that

NaOH precipitates manganese, nickel, and cobalt, while NH_4OH does not. This occurs with manganese because of the far greater concentration of hydroxide-ion in the NaOH solution, and with nickel and cobalt partly on this account and partly because there is no complex formation, as there is with NH_4OH. $Mn(OH)_2$ is white, but rapidly turns brown owing to oxidation to $Mn(OH)_3$; $Ni(OH)_2$ is light green, $Co(OH)_2$ is pink, but from cobalt solutions a blue basic salt is first precipitated in the cold. If a large excess of NaOH be added, a little $Co(OH)_2$ dissolves yielding a blue solution, doubtless forming a salt such as Na_2CoO_2. This is to be avoided since then the cobalt will not be completely oxidised and precipitated upon the subsequent addition of Na_2O_2.

6. By the addition of Na_2O_2, $Fe(OH)_2$ is changed to dark red $Fe(OH)_3$, $Mn(OH)_2$ to brown hydrated MnO_2, $Co(OH)_2$ to black $Co(OH)_3$, $Ni(OH)_2$ partially to black $Ni(OH)_3$, and thallium is precipitated as dark red $Tl(OH)_3$, all of which are insoluble in excess of NaOH and remain, together with $TiO(OH)_2$ and $ZrO(OH)_2$, in the precipitate. Chromium and uranium, which after the addition of NaOH are present as soluble sodium chromite or as insoluble sodium diuranate, $Na_2U_2O_7$, are converted by Na_2O_2 into chromate, Na_2CrO_4, and peruranate which are soluble compounds, and remain in solution, together with the zinc, beryllium, and vanadium. which are still present as zincate, beryllate, and vanadate. The separation is more satisfactory, especially in the case of uranium when a large amount of Na_2O_2 is used.

7. Even a cold solution of Na_2O_2 decomposes rapidly with evolution of oxygen, and this decomposition takes place with explosive violence when the solution is hot. The peroxide is therefore added in small portions to the cold solution. A steady evolution of gas continuing after the mixture has been well-stirred is an indication that sufficient peroxide has been added. The mixture is finally boiled in order to destroy the excess of Na_2O_2, and to cause the complete precipitation of titanium, some of which first passes into solution, probably as the pertitanate. The solution is cooled because $Tl(OH)_3$ is somewhat more soluble in the hot solution than in the cold one. Even in the cold when thallium is present alone about 0·5 mgrm. will usually pass into the filtrate, but precipitation is complete when elements of the iron group are also present. The solution is diluted before filtering in order to avoid the disintegration of the filter-paper; it is often advantageous to support the filter by folding it together with a small hardened filter.

8. The Na_2CO_2 is added to cause the complete precipitation of the alkaline earth elements, whose hydroxides, especially that of barium, are somewhat soluble even in the presence of NaOH. $ZnCO_3$, though insoluble in a dilute solution of Na_2CO_3 alone, dissolves when much NaOH is present, owing to the nearly complete conversion of the zinc-ion into zincate-ion by the reaction $Zn^{++} + 4OH^- = ZnO_2^= + 2H_2O$. The Na_2CO_3 also serves to decompose the chromates of the alkaline earth elements; if it is not added, chromium may remain in the precipitate and escape detection. It is unnecessary to add the Na_2CO_3 when the alkaline earth elements are known to be absent.

9. Phosphate or oxalate, if present, divides itself in this procedure between the precipitate and solution in a proportion which depends on the nature and quantities of the metallic elements. (See P. 51, N. 6). Their presence does not cause any of the elements to precipitate which would not otherwise do so, in spite of the slight solubility of aluminium, zinc, and beryllium phosphates. This is due to the fact that the cations of these elements (Al^{+++}, Zn^{++}, Be^{++}) are present in the NaOH solution only at an extremely small concentration, owing to their combination with the OH ion to form anions, (AlO_2^-, $ZnO_2^=$, $BeO_2^=$).

10. Even when less than 1 mgrm. Cr is present as chromate, it imparts a distinct yellow colour to the alkaline solution, so that when a colourless solution results, it proves the absence of this element. Uranium in small quantity also gives a yellow colour to the solution, which is noticeable with 1 or 2 mgrms.; a moderate amount (about 10 mgrms.) gives a red colour, which is intense with still larger quantities. Alkaline solutions containing vanadium are colourless after boiling.

11. This separation with NaOH, Na_2O_2, and Na_2CO_3 is a very satisfactory one, except in the case of zinc. This element, when present in small quantities, is completely carried down in the precipitate when much iron, nickel, or cobalt, or especially manganese, is present. Provision for the detection of zinc in the precipitate must therefore be made.

12. If Na_2O_2 is not available, sodium hypobromite, NaBrO (prepared by mixing NaOH and bromine, as described in P. 70, N. 3), may be used as the oxidising agent, but it is not quite so satisfactory as Na_2O_2, for it does not oxidise $Cr(OH)_3$ so readily, and it is apt to oxidise some of the manganese to $NaMnO_4$ (especially if there is not a sufficient excess of NaOH present).

**Procedure* 52*a*.—To detect rare earth elements, and to remove them, if present, transfer the acid solution (P. 52) to a platinum dish (after destroying HNO_3, if any has been added, by evaporating in porcelain once or twice with HCl, 1·20), and evaporate just to dryness, Add to the residue 45 per cent HF solution, little by little, until the residue has been dissolved, or until about 25 cc. have been added, stirring with a platinum rod after each addition, and finally boiling gently under a hood for a minute or two if there is still a residue. Collect the residue on a filter supported on a platinum ring or in a celluloid funnel; collect the filtrate in a platinum dish, wash the residue thoroughly with water.

To the filtrate add 3 to 5 cc. HCl (1·20), and evaporate it just to dryness; add a little HCl, and evaporate again, and repeat these operations a third time. Dissolve the residue in a little water, adding HCl if necessary; transfer to a casserole, and treat the solution by the last paragraph of P. 52, first evaporating with HNO_3 to destroy HCl if chromium, uranium, and vanadium are to be tested for by *P. 58*a*—*e*.

Transfer the residue insoluble in HF to a platinum crucible; if the filter has been added, ignite to destroy it. Add 2 to 5 cc. H_2SO_4 (1·20), heat until sulphuric acid fumes are given off, cool, add 10 to 20 cc. water, heat, and filter. Treat the precipitate (which can consist only of $CaSO_4$, $SrSO_4$, or $BaSO_4$) with concentrated Na_2CO_3 solution by P. 6. To the H_2SO_4 solution add ammonia until alkaline. (White precipitate, presence of *rare earth elements*). Filter, and test the filtrate for calcium and magnesium. Wash the precipitate thoroughly, dissolve it in a little HCl, evaporate just to dryness in a platinum dish, dissolve in a little water, and add 5 to 10 cc. HF. (White precipitate, presence of *rare earth elements*).

Notes.

1. Among the so-called rare earth elements are included thorium, cerium, lanthanum, praseodymium, neodymium, yttrium, ytterbium, and a number of other similar elements. These elements, like the alkali earth elements, are characterised by the insolubility of their fluorides, but differ from the alkali earth elements in that their hydroxides are precipitated by ammonia, and that their sulphates are not precipitated by sulphuric acid. It is upon these facts that the separation described in the above procedure is based. If there is no residue after the treatment with HF, it shows, of course, that the rare earth elements are absent; if, on the other hand, there is a residue, it does not necessarily show their presence, except when it is known that alkaline earth elements cannot be present. (See P. 51, N. 6 and 7). The further treatment described in the procedure serves to eliminate the latter.

2. Owing to the fact that aluminium and chromium fluorides are somewhat difficultly soluble in HF, care must be taken to use a rather large quantity of this acid

when a residue remains. It is also obvious that the fluoride residue must be thoroughly washed if the formation of a precipitate with ammonia is to be considered a conclusive indication of rare earth elements. The final treatment of the NH_4OH precipitate is recommended to eliminate the possibility of error from these sources.

3. The HF solution, which may contain all the elements of the aluminium and iron groups, is evaporated repeatedly with HCl to expel the HF, which is especially apt to be retained when titanium and zirconium are present.

(To be continued).

NOTICES OF BOOKS.

Synthetic Inorganic Chemistry. By ARTHUR A. BLANCHARD, Ph.D. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1908.

THE preparation of inorganic compounds of commercial importance is well treated in this little book, which has much to recommend it as an introduction to qualitative analysis. The principles and methods employed in synthetical chemistry are illustrated by well chosen examples, and a general discussion of the essential features of each preparation is followed by directions for the experimental work, which are invariably given separately; thus the student has no excuse either for losing sight of the theory of the reactions owing to the abundance of experimental details on the one hand, or for neglecting practical precautions on the other. Finally, questions bearing upon each preparation are propounded, most of them well selected, though perhaps a trifle difficult for the students for whose use the book is intended, and in addition there are sets of questions relating to the whole group of metals previously treated; in some cases these include simple supplementary practical problems, and these general questions make considerable demands upon the reasoning power and knowledge of the student. There can be no doubt about the value of working through such a course as that given in this book as an introduction to analysis, but it is perhaps debatable whether the average student could spare the time for it; it is not impossible, however, that the better grasp of the fundamental principles of analysis which he ought to acquire from a systematic study of the synthesis of compounds of each group of metals might actually save him time in the end.

Spectrum Analysis. By JOHN LANDAUER, Ll.D. Translated by J. BISHOP TINGLE, Ph.D., F.C.S. Second Edition. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1907.

THIS book gives an account of the use of the spectroscope and special spectroscopic instruments and appliances, and contains all that is required for ordinary analytical purposes; the spectra of the elements are tabulated and absorption spectra are also treated. Rowland's table of the wave-lengths of the Fraünhofer lines is reproduced in full, and some account is given of the spectra of celestial bodies other than the sun, of the aurora borealis, zodiacal light, lightning, &c. In the new edition the descriptions of some of the older instruments are replaced by those of more modern forms which have been found superior in practice, and also the measurements of spectra have been revised, the values being taken from Watts' "Tables of Spectra."

A Pocket Handbook of Minerals. By G. MONTAGUE BUTLER, E.M. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1908.

THIS book is intended to be used in field work, and also as a supplement to lectures on mineralogy. It lays special stress upon the identification of minerals by means of their physical properties, and the arrangement is such that the user should be able by help of the information given to decide the name of an unknown mineral without much possibility of doubt. Plenty of space is left for the insertion of additional notes upon the various minerals, and some illustrations are given. Simple chemical tests are also occasionally described, mostly as regards the behaviour of the mineral before the blowpipe and upon the addition of dilute acids, but from the aim of the book these are not given so much prominence as physical methods of identification. The minerals are arranged according to chemical composition, and some notes on their uses and value are added.

Les Nouveaux Livres Scientifiques et Industriels. ("New Scientific and Industrial Books"). Volume I. Years 1902 to 1907. Paris: H. Dunod and E. Pinat. 1908.

THIS well arranged bibliography will be a boon to French engineers, manufacturers, and scientific men generally. It gives first a general alphabetical list of books published in the French language during the years 1902—1907 dealing with technical and scientific subjects. This complete index to the whole volume is followed by an alphabetical list of authors, while the bibliography proper occupies the greater portion of the book. It is divided into twenty parts, published quarterly, and each part is separately indexed. For every book the title, author's name, price, size, and number of pages are stated, together with a short *résumé* of the contents, and the catalogue thus gives every possible assistance to scientific men who wish to keep abreast of modern developments in any particular subject in which they are specially interested.

CORRESPONDENCE.

WOMEN AND THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—As one of the signatories to the petition to the Council of the Chemical Society, I regret that the issue of a letter dated from Oxford, July 1st, 1908, by eleven of our most distinguished chemists, in which the petition is stated to be a declaration of opinion, renders it necessary to point out that it was signed by myself, and I believe many others, as a petition to the Council to ascertain the wishes of the Society on the question, and not as a petition for the admission of women.

I regret still more that the perfectly natural choice of the Society's printers for the printing of the letter and petition has led to the use of the same paper and type as the Council's circular, and of the official address labels, and has therefore doubtless in many cases caused the impression, until this was corrected by the Officers of the Society, that the Oxford letter signed by so many Past-Presidents and the petition were officially issued to show how great was the support.

Since signing the petition I have given much consideration to the question, and greatly sympathise with those women chemists who are debarred from the privileges of the Fellowship, and if there were nothing beyond the mere question of allowing them to vote, to use the Library, and to receive the Journal, I should unhesitatingly do all I could to further their admission.

Unfortunately there is a very grave issue beyond this, and as it is not mentioned in the very fair and impartial statement of the arguments on both sides issued by the Council, I venture to outline it.

Women being the weaker—I do not say inferior—sex have many privileges of courtesy, and if they are granted the full privileges of the Fellowship will have an advantage over men. I can perhaps make my meaning clearer by an example:—An unknown woman reading her first

paper before the Society will be listened to with an attention which would be denied to an unknown man, and more consideration would be given to it by the Publication Committee, and the reading and publication of the first paper is often an important step in a chemist's career. In this way the woman would have an advantage over the man, and might eventually gain an appointment, not upon merit alone, and displace a man; as a man generally supports a woman who has taken up the profession for which Nature has best fitted her—that of maternity—the woman chemist would in the long run displace a man, another woman, and their children. When I have to consider the interests of women, there is only one woman who really counts—my wife—and seeing that by voting for the admission of women to the Fellowship I may possibly be furthering the interests of another woman to the detriment of those of my wife, my sympathy for women chemists is greatly weakened.

The position of the distinguished chemists who signed the Oxford letter is such that they could not be displaced by any one, and consequently the above view has never probably occurred to them, and it is doubtless only a feeling of chivalry that has led them to issue their circular independently of the Council of which they are members, but I venture to think that the humble rank and file of the profession like myself will view the subject in a different light, and fear that the same feeling of chivalry will induce the leaders of the profession to give undue advantages to women should they be admitted as Fellows.

As after careful consideration of the whole question, I have now become an opponent of the admission of women, I would like to thank Dr. Divers for the admirable way in which he has given his side away; it requires little more testimony of the weakness of his case when a confession is made that the issue of a statement of the arguments for and against the admission of women is an unfair advantage to the opponents of the measure; when the omission of the obvious fact that the supporters of admission of women think that the time has now come for that to be accomplished is called still more unfair advantage to the opponents, the position becomes ludicrous; and when the Council, after presumably a full discussion of the subject, is supposed to have no official cognisance of the nature of the arguments against the admission of women, and the Secretaries are blamed when by order of the Council they issue a circular containing what is obviously an abstract of the discussion, it appears that what the supporters of the measure most dread is a full statement of the case on both sides being placed before the Fellows for their unbiassed consideration.

I would appeal to Fellows not to be influenced by the support that our most illustrious chemists have given to the movement, as their very eminence prevents not only their being able to view the whole subject, but also their interests being affected one way or the other, but to weigh carefully the arguments on both sides, and come to an independent decision.—I am, &c.,

H. DROOP RICHMOND.

London, July 20, 1908.

EXPLOSIVE CRYSTALLISATION.

To the Editor of the Chemical News.

SIR,—Is not the true explanations of the mishaps described in issue of July 17 to be found in the fact that the vacuum was too great for the resistance to crushing of the glass receivers and plates, and that it was the pulsations of these yielding to continued over-exhaustion before they snapped that caused the bumping? Had the air-pump been a copper still or a vacuum pan they might have been flattened, *i.e.*, if they were as unequal to the strain as these receivers and plates prove themselves to have been. It was just as well the pressure was from outside to inside instead of from inside to outside. In the latter case the consequences might have been serious. It must be acknowledged that 19 mm. from an absolute vacuum is very nigh 15 lbs. to the square inch, so the total pressure on the outside of receiver and plate was several hundredweights. Are ordinary air-pumps made to stand such highly diminished internal pressure? I imagine not. Whether there was sudden absorption of heat at the moment of crystallisation, if crystallisation occurred *en masse* and suddenly cooled, the remaining volume of highly attenuated air can easily be ascertained by the physical chemistry of the substance used. But that for the moment I have no time to consider. In any case the pulsation causing bumping seems to debar the effects of sudden condensation.—I am, Sir, &c.,

JOHN GEDDES M'INTOSH.

9, Parsonage Street, Cubitt Town, E.

POTENTIAL ENERGY OF THE ELEMENTS.

To the Editor of the Chemical News.

SIR,—I regret that through an error in transcribing, the potential given in my paper on "The Potential Energy of the Elements" (CHEMICAL NEWS, xcvii., p. 302), for tellurium, viz., 3228 should be 3288; a note should also have been appended stating that this was the potential of the theoretic element having a density 6·045 and atomic weight 124·57. The potential for tellurium, which I consider to be a compound of two elements, is 3137 K.

I would also remark that, in my view, tellurium cannot be split up into its components by ordinary chemical analysis, the energy reactions by this method being on too low a grade.

Tungsten is another compound element of an analogous nature to tellurium.—I am, &c.,

DANIEL J. RANKIN.

Orleans House, Peterborough,
July 21, 1908.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. cxlvi., No. 26, June 29, 1908.

Decomposition of Alcohols under the Catalytic Action of Live Coals.—Georges Lemoine.—When live coals from a baker's oven are heated to redness and then allowed to act on alcohol at temperatures ranging from about 380° to 440° the decomposition of the alcohol is of the nature of a dehydrogenation, instead of dehydration, as with purified animal charcoal. Isopropyl alcohol, however, is an exception, and differs in its behaviour from normal propyl alcohol. This difference in the effect of animal charcoal and coal shows how different transformations can be effected by slightly different substances. The phenomena observed confirm the general law that catalysers lower the temperature of chemical transformations.

Action of Metallic Oxides on Primary Alcohols.—Paul Sabatier and A. Mailhe.—The authors have allowed the vapours of primary alcohols to act upon a number of different metallic oxides at temperatures between 350° and 400°. They find that the oxides can be divided into four classes according to their behaviour under these conditions: 1. Those which below 400° undergo no reduction and have no appreciable effect upon alcohols; these include calcium, barium, and strontium oxides, calcined magnesia, calcined silica, and titanic oxide TiO_2. 2. Those which are rapidly reduced to metal or lower oxide. 3. Those which are not reduced at temperatures below 400°, but act catalytically, yielding either aldehyde or ethylene hydrocarbon, or both. 4. Those which react only slowly and cause the condensation of the alcohol.

Preparation of Alkaline Chloroiridites.—M. Vèzes.—The author calls attention to the fact that the preparation of alkaline chloroiridites by reduction of the chloroiridates with neutral oxalate, described by M. Delépine (*Comptes Rendus*, June 15, 1908, cxlvi., 1267) is not new, but was reported seven years ago (*Procès-verbaux des Séances de la Société des Sciences Physiques et Naturelles de Bordeaux*, July 18, 1901, p. 112).

Molecular Weights of Phosphoric Acids determined by Cryoscopy.—H. Giran.—In acetic solution the molecular weight of metaphosphoric acid diminishes with the time, and tends towards a limit which is lower the more dilute the solution. The molecular weight of the meta acid is 400 and the formula is $(PO_3H)_5$. The same holds good for pyrophosphoric acid, which has the formula $(P_2O_7H_4)_3$ and the molecular weight 534. With the ortho acid the molecular weight varies with the time, all the results being included between the normal weight $PO_4H_3 = 98$ and the normal weight $(PO_4H_3)_2 = 196$. This might be interpreted by supposing that the limit is reached very rapidly. The molecular condensation of the ortho acid is the same in the liquid and solid state, and the condensation is certainly greater than 1. It is logical to conclude that the diminution of molecular condensation observed in passing from the meta to the pyro acid is continued when we pass from the pyro to the ortho acid. The last should then have a condensation lower than 3, and thus equal to 2. Thus solid or liquid orthophosphoric acid must be represented by the formula $(PO_4)H_3)_2$.

Tellurides of Arsenic and Bismuth. Cryoscopic Constant of Tellurium.—H. Pélabon.—Fused tellurium dissolves easily in arsenic. The liquid obtained is grey when little arsenic is present, and darkens gradually to black as the proportion of arsenic increases. The temperature of sodidification of the liquid decreases rapidly and regularly from 452°, the melting-point of tellurium, to 329°, the temperature of solidification of the mixture formed of 3 atoms of tellurium to 1 of arsenic. If the proportion of arsenic is increased the temperature of solidification rises, reaches a maximum value 362° for the compound As_2Te_3, then falls, becomes 355° for the mixture $9As + 11Te$, and again rises to 358° for all mixtures containing more than 1 atom of arsenic to 1 of tellurium. The fusion curve of mixtures of tellurium and bismuth from the melting-point of tellurium, 452°, has first an almost rectilinear part, which ends at 410°, corresponding to the eutectic mixture containing about 15 per cent of bismuth. From this point for mixtures richer in bismuth, the temperature of solidification increases, and reaches a maximum at 583° for the compound Bi_2Te_3. It then falls regularly to 263°, which is the solidification-point of the eutectic containing 1 per cent of tellurium. The temperature of solidification then increases to 270°, which is the melting-point of bismuth. Thus, if a small quantity of arsenic or bismuth is added to tellurium, compounds As_2Te_3 and Bi_2Te_3 are formed, and dissolve in the excess of tellurium. The study of the solidification of these solutions shows that the cryscopic constant of tellurium is 520.

Mechanism of Synthesis of Nitrogen Cycles.—L. J. Simon.—The action of pyruvic acid on paratoluidine gives a product,—

$$CH_3—\underset{\displaystyle NH—C_7H_7}{\overset{\displaystyle CO_2H}{\overset{|}{C}}}—CH_2—\underset{\displaystyle NH—C_7H_7}{\overset{\displaystyle C(OH)—CO_2H}{\overset{|}{C}}},$$

formed by the condensation of two molecules, $CH_3—\underset{\displaystyle NH—C_7H_7}{\overset{\displaystyle C(OH)—CO_2H}{\overset{|}{C}}}$. The action of water upon this substance may be represented by the two equations $C_{20}H_{24}N_2O_5 = C_{12}H_{11}NO + CO_2 + H_2O + H_2 + C_7H_7NH_2$, $C_{20}H_{24}N_2O_5 = C_{19}H_{22}N_2O_2 + CO_2 + H_2O$. The first substance formed is 2-6-dimethylquinoline carbonic acid. The second product is a cyclic compound formed by the removal of OH_2 and CO_2 from the COOH, NHC_7H_7, and CO_2H groups of the original condensation product.

Messinger and Vortmann's Method of Estimating Phenols.—J. Bougault.—The author has shown that Messinger and Vortmann's method of estimating phenols gives with salicylic acid a compound which has always the composition $(C_6H_2I_2O)_x$, and which is identical with Lautemann's "red substance." The formation of this substance can be utilised to separate and determine salicylic acid. The constitution of the red substance seems to be $\begin{vmatrix} C_6H_2I_2O \\ C_6H_2I_2O \end{vmatrix}$, *i.e.*, it may be called tetraiododiphenylene-quinone.

Three New Primary Methods resulting from the Condensation of Sodium Benzylate with Propyl, Butyl, and Isoamyl Alcohols.—Marcel Guerbet.—Sodium benzylate reacts with propyl alcohol giving an alcohol of formula $C_{10}H_{14}O$. This is methylbenzylethyl alcohol, $C_6H_5—CH_2—CH(CH_3)—CH_2OH$, and the same reaction occurs with butyl and isoamyl alcohols:—

$$C_6H_5—CH_2ONa + C_4H_9OH = C_6H_5—CH_2—C_4H_8OH + NaOH,$$

$$C_6H_5—CH_2ONa + C_5H_{11}OH = C_6H_5—CH_2—C_5H_{10}OHNaOH.$$

The first alcohol is ethylbenzylethyl alcohol, $C_6H_5—CH_2—CH(C_2H_5)—CH_2OH$, and the second is probably isopropylbenzylethyl alcohol,—

$$C_6H_5—CH_2—CH(C_3H_7)—CH_2OH.$$

Researches on Diazo Compounds.—H. Duval.—The author has studied the action of nitrous acid upon the following orthodiamino compounds—of diphenylmethane *p*-*p*-dicarbonic acid, diphenylmethane *p*-*p*-dinitrile, *p*-*p*-diacetyldiphenylmethane, diphenylmethane, diacetyldiaminodiphenylmethane. The first three compounds give only a diazo compound, while the last two yield phenol and diazo compound in varying proportions according to the experimental conditions. Of these compounds some, *e.g.*, the diazo compound of diphenylmethane dicarbonic acid, fuse at a temperature above 300°, while others, for instance diazodiacetyldiphenylmethane, decompose on heating.

Products of Condensation of Chlorides of *o*- and *p*-Nitrated Benzile with Acetylacetone.—M. Mech.—*p*-Nitrated benzile chloride gives with acetylacetone the disubstituted derivative—

$$CH_3COC\begin{cases} CH_2^{(1)}C_6H_4^{(4)}NO_2 \\ COCH_3 \\ CH_2^{(1)}C_6H_4^{(4)}NO_2 \end{cases},$$

and also *p*-nitrophenylbutanone—

$$CH_3COCH_2CH_2^{(1)}C_6H_4^{(4)}NO_2,$$

of which the semicarbazone has been prepared. The corresponding compound from ortho-nitrated benzyle, *o* nitrophenylbutanone, has not been isolated, but its oxime and semi-carbazone have been prepared, and evidently the ortho compound reacts in exactly the same way as the para compound with acetylacetone.

COUNTY COUNCIL OF DURHAM.

DARLINGTON LOCAL COMMITTEE—TECHNICAL COLLEGE.

Wanted, an ASSISTANT LECTURER qualified to teach Chemistry, Metallurgy, Mineralogy (including Iron and Steel Manufacture), Geology, and allied subjects. Form of application, scale of salaries, and particulars of duties from the undersigned; the former to be returned not later than AUGUST 21st, 1908.

A. C. BOYDE,
Local Secretary.

Education Office,
North Lodge, Darlington,
July 24th, 1908.

THE CHEMICAL NEWS.

Vol. XCVIII., No. 2541.

THE MECHANISM OF MOTION.

By JOHN McDOWALL, F.C.S.

For some time I have been engaged on the study of some of the problems of motion, and the conclusions which I have formed may be of some interest to your readers.

The main difficulty I have experienced is to form a mechanical conception of motion.

Suppose, for instance, we apply motion to a projectile so that it moves for a distance through space, we suppose it to be charged with an occult principle called energy, on account of which it is enabled to diminish or increase the space between itself and other objects.

Now this operation, like all other phenomena in Nature, must have a mechanical foundation, and must work according to laws which can be understood, and in the foregoing example I confess that it is impossible to form a mechanical conception of how a body charged with any occult principle can move through space faster than other bodies which have not received the same initial quantity of energy.

Now, I have been able by looking at the matter from a completely different point of view to form a mechanical conception of motion, and in addition the inferences founded on this view explain in a very plausible way some of the difficulties of physicists.

Suppose the fundamental unit in the atom to be a species of wave which moves at a speed proportional to its propagation. Matter would then be fundamentally a state of the ether which was handed on—nothing would move through the ether in the sense of a body moving through a liquid, but a state would move through it.

If we look at the matter from this point of view we can form a mechanical conception of how motion takes place.

The ether acts as a continuous medium on account of which the state which we have assumed to be matter can move mechanically along, and this without resistance no matter how dense the ether may be.

It might be a thousand times more dense than steel, and still matter would be able to flit like a shadow through it without resistance.

The reader will probably have some difficulty in detaching himself from the erroneous impressions of the senses and look at the matter from a purely abstract point of view.

We are accustomed to see the superficial working of motion from our childhood, and we see a projectile moving through the air without any mechanical bases for its motion, and conclude instinctively that as the projectile moves through the air in like manner the fundamental unit of matter moves through the ether: familiarity has destroyed the power of looking at the matter from the point of view of pure reason.

Reasoning from this starting point we regard the atom from a different point of view. It may be that the atom is composed of corpuscles, and it may be that these corpuscles are in their turn composed of others, but the fundamental unit, however it may be combined, is a species of wave which moves at a speed proportional to its compression, as it is as inconceivable that motion can take place without a mechanical basis as the old idea of action at a distance, and is a fallacy of the senses.

When we make a body move, the motion is transmitted to it in the form of a large wave in the matter which connects the body with the source of the impulse, and this large wave distributes itself over all those little fundamental waves which constitute matter, reinforcing them, and the body as a whole on account of the greater compression of the fundamental waves moves on with an increased speed, and the difficulty in overcoming the elasticity of the ether in altering the state of compression of the fundamental unit produces an initial difficulty in starting the body, which is known as inertia.

There are some difficulties which at first sight are not easy to explain.

It is not easy to conceive how such an elusive thing as a wave can combine to form a rigid body. In order to explain this we have to look on the fundamental unit as a centre of distortion in the ether—the ether surrounding it must be in a state of strain, as a part of it is under compression or distortion of some kind, and it is to this strain that I attribute the rigidity of matter; the fundamental units tend to settle down in the vicinity of each other in a position determined by the strain in the ether which surrounds them.

Again, rigidity is a relative term; we have no absolute measurement for rigidity, we simply compare the rigidity of one kind of matter with another. In those circumstances the forces holding matter together compared with such things as the rigidity of the ether might be of the feeblest description, like bubbles held together by surface tension on the surface of a pond; what would be a gentle shake compared with those other forces would completely vapourise matter.

Sir Oliver Lodge, in his calculations on the density of the ether, has shown in a striking manner the order of magnitude of the weight of the ether, and the energy which it contains is probably of the same order, which is much vaster than what can be displayed by matter.

The ether, in fact, has unique properties of its own, and we cannot look upon it as obeying the same laws as matter, though it is possible to deduce its properties by reasoning.

The results of my investigation may be summed up in this, "That motion can only be transmitted through the agency of a conducting medium;" so if in any part of space there was a break or hole in the ether it would be impossible for matter or any form of motion to pass through it, just as it would be impossible for sound to pass through a vacuum.

Sebaieh, Upper Egypt.

THE DECOMPOSITION OF CERTAIN MINERALS AND INDUSTRIAL PRODUCTS BY MEANS OF SODIUM PEROXIDE AND METALLIC SULPHIDES.*

By JAMES H. WALTON, Jun., and HERMAN A. SCHOLZ.

In the year 1893 J. Clark (*Journ. Chem. Soc.*, 1893, liii., 1079—1083) published a method for decomposing pyrites, zinc blende, galena, chromium, and arsenic ores by mixing them with sodium peroxide in an open platinum or nickel dish and fusing in the usual manner. W. Hempel (*Zett. Anorg. Chem.*, 1893, iii., 193) used a similar method for the decomposition of chromium, manganese, tungsten, and titanium ores. Spüller and Kalman (*Chemiker Zeitung*, 1892, xvii., 881, 1207, 1360, 1412; 1893, xviii., 292), Edinger (*Zeit. Anal. Chem.*, 1895, xxxiv., 362), Saniter (*Chemiker Zeitung*, 1898, xix., 1657), Glaser (*Journ. Am. Chem. Soc.*, 1898, xx., 130), Angenot (*Zeit. Angew. Chem.*, 1904, xvii., 1274), and Lucchese (*Ann. Chim. Anal. Appl.*, 1905, ix., 450) used sodium peroxide for the decomposition of various organic and inorganic substances. These investigators all followed the method of placing the substance to be decomposed in a crucible, mixing with sodium peroxide, and applying heat to the crucible. While the decompositions made in this way are very complete, the sodium peroxide attacks the crucible

* *American Chemical Journal*, xxxix., No. 7.

vigorously, and a large amount of foreign matter is consequently introduced into the determination.

A number of investigators have published methods of decomposition in which the heat necessary to bring about the decomposition is furnished by the reaction between the peroxide and some organic substance present in the mixture. S. W. Parr (*Journ. Am. Chem. Soc.*, 1900, xxii., 646) decomposed coal by mixing it in a steel bomb with sodium peroxide and igniting the mixture by dropping a red-hot iron wire into the mass, the combustion taking place without further application of heat. Although this method was used primarily for the determination of the heating power of coals, it was found that the sulphur was completely oxidised to the sulphate and could be determined in the usual manner.

Pringsheim (*Am. Chem. Journ.*, 1903, xxxi., 386; *Ber.*, 1904, xxxvii., 2155; 1906, xxxviii., 2436) used a similar method for the quantitative and qualitative determination of the halogens, arsenic, and phosphorus in organic compounds. Von Konek (*Zeit. Angew. Chem.*, 1904, xvii., 771, 1093) also used this method for making qualitative analyses of organic substances, using a cylindrical nickel or steel crucible similar to that designed by Parr for use in his calorimeter. The finely powdered sample, in this case, was mixed with sodium peroxide and a compound rich in carbon, such as camphor, and the mass ignited by dropping in a red-hot iron wire.

The decomposition of substances by means of the heat obtained from the action of the sodium peroxide on an organic compound mixed with the substance has several advantages. In the first place, the vessel in which the decomposition is carried out is attacked to an extent which is for many purposes inappreciable. Moreover, the decomposition is completed in a very few minutes. It seemed to the authors that this method could be modified and used to decompose certain substances of technical importance, particularly those which require the use of nitric acid for their decomposition, the excess of which must often be removed by evaporation with sulphuric acid before the determination can be made.

Experimental.

The sodium peroxide used in these experiments was the ordinary commercial article manufactured by Koenig and Co. It contained traces of SiO_2, Al_2O_3, and Fe_2O_3. Its purity was determined by measuring the volume of oxygen which was given off from a weighed amount of the substance when decomposed by water containing a few drops of a dilute solution of cobalt nitrate (Archbutt, *Analyst*, 1895, xx., 3).

The sample used in this work contained between 95 and 96 per cent sodium peroxide.

The Decomposition of Substances containing Lead

a. Galena Ores.—Two galena ores were used in testing this method of decomposition. The percentage of lead present was first determined gravimetrically by boiling the finely ground ore (passed through a 200-mesh sieve) with concentrated nitric acid and a small amount of hydrochloric acid for one and a-half hours, precipitating the lead as the sulphate, filtering, separating the lead sulphate from the residue by dissolving in hot ammonium acetate solution, re-precipitating by means of sulphuric acid, and weighing the lead sulphate on a Gooch crucible.

The following values were obtained :—

Per Cent of Lead.

	1.	2.
Ore No. 5	61·58	61·52
Ore No. 22	56·05	55·98

These iron ores contained a small amount of iron pyrites and a little silica. Long boiling with acid was found to be absolutely necessary to completely decompose them. In one case in which the ore was boiled for only one-half hour, results were obtained which were several per cent lower than those given above. The above results were taken as the true values for these ores, as they agree with analyses made later by different methods.

For the purpose of determining the right kind of sodium peroxide mixture to decompose these ores, a number of qualitative experiments were made in which the ores were placed in the bomb of a Parr calorimeter and mixed with sodium peroxide and various easily oxidisable substances, such as magnesium, ammonium oxalate, and starch. The thoroughly mixed charge was ignited by dropping a red-hot piece of iron wire into the water-cooled bomb. When starch was used the mass fused quietly. It was found that the addition of a small amount of potassium persulphate to the sodium peroxide gave a better fusion and an apparently complete decomposition of the ore (S. W. Parr, *Journ. Am. Chem. Soc.*, 1902, xxiv., 167).

The following quantitative experiment was carried out :—

Experiment I.

0·3 grm. ore No. 5 (200-mesh sieve); 5·0 grms. sodium peroxide; 0·2 grm. starch; 0·3 grm. potassium persulphate.

This mixture was ignited in a closed bomb by means of a fine iron wire which passed through the charge, and which was heated to a red heat by means of an electric current. The melt was dissolved in 100 cc. of water and enough sulphuric acid added to neutralise the alkali and leave an excess of 2 per cent acid. Sodium bisulphite was added to reduce the lead peroxide, and the solution was boiled for five minutes. It was then diluted and the lead determined gravimetrically as the sulphate.

The following results were obtained :—

Per Cent of Lead.

Ore No. 5 ..	57·49	60·22	59·13

In these experiments it was observed that the fusion did not take place quietly, but was attended by slight explosions, which threw the fused mass upon the side of the bomb. It seemed reasonable to believe that this fact might be the cause of the low results.

Zinc sulphide, when mixed with sodium peroxide and ignited, is oxidised with the evolution of great heat, the oxidation taking place quietly however. The following quantitative experiment was made in which this substance was substituted for the starch. The zinc sulphide used was the dry, finely divided product prepared by Kahlbaum.

Experiment II.

0·5 grm. ore; 8·0 grms. sodium peroxide; 0·8 grm. zinc sulphide; 0·3 grm. potassium persulphate.

The mixture was placed in an open bomb and ignited as before. The entire mass became liquid and red-hot, and the fusion took place without any spattering. The following results were obtained :—

Per Cent of Lead.

	1.	2.
Ore No. 5	60·61	59·73
Ore No. 22	55·51	55·18

In this series the lead sulphate was determined by titrating the ammonium acetate solution of lead sulphate with ammonium molybdate according to Alexander's method (*Eng. and Min. Journ.*, xiii., 55; see also *Bull. School of Mines Quarterly*, 1902, xxiii., 348), the melted mass from the fusion being treated in other respects as in Experiment I. The results obtained in the analysis of the two ores are somewhat better than those obtained when starch was used, but they are from 0·5 to 1·00 per cent lower than the values obtained by the acid decomposition method.

In several cases in which the above charge was used the decomposition was found to be incomplete, a slight amount of the ore remaining undecomposed in the sharp edge of the bomb at the point at which the wall and bottom intersect. It was apparent that this part of the bomb did not become sufficiently hot to decompose the

ore. Since the fusion takes place quietly, it was found possible to avoid this uncertainty of decomposition by using a nickel crucible which has rounded edges, and consequently affords no place for the ore to lodge. Moreover, the melt could be more easily removed and less water was needed for its solution. The nickel crucible used had a capacity of 30 cc. and was 1¾ inches in diameter. The charge was placed into the crucible and ignited by means of a short piece of magnesium ribbon instead of iron wire, which caused considerable trouble by forming the magnetic oxide of iron. This compound, being difficultly soluble, remains as a residue and makes it very difficult to tell whether or not the ore is completely decomposed.

Experiment III.

The charge used was the same as in Experiment II. The dry, finely ground sodium peroxide was measured by means of a small aluminium scoop. The other substances were added and thoroughly mixed by means of a glass rod, which was then brushed clean. The cover was placed upon the crucible and was moved far enough to one side to permit the dropping in of a piece of lighted magnesium ribbon about one-half inch in length.

After the ignition had taken place the crucible was immediately covered. The lead was determined by the molybdate method, the following results being obtained :—

Per Cent of Lead.

	1.	2.
Ore No. 5	61·23	61·22
Ore No. 5 (gravimetrically).	60·68	59·07
Ore No. 22	55·82	55·68

These low results might be due to incomplete decomposition, although, from the fact that no residue could be seen on dissolving the fusion in acid, this seemed improbable. To test this point, however, a sample of the ore was fused with sodium peroxide in an iron crucible, the heat being supplied by a Bunsen burner.

Experiment IV.

0·3 grm. ore No. 5 ; 5·0 grms. sodium peroxide.

This mass was kept in a molten condition for five minutes and the lead determined gravimetrically. The results were low, 60·07 and 60·06 per cent of lead being found in duplicate determinations.

It will be seen that the results obtained with ore No. 5, in Experiments II., III., and IV., vary between 59·07 and 61·23. It was noticed that in the experiments in which the lowest results were obtained, the precipitate of lead sulphate was coloured dark brown, due to basic sulphates of iron which are precipitated upon boiling in a slightly acid solution when large quantities of alkali salts are present (Pickering, *Journ. Chem. Soc.*, 1880, xxxvii., 807). It occurred to the authors that these basic iron salts kept the lead sulphate from being dissolved by the ammonium acetate solution, the effect being similar to that produced by the presence of barium sulphate (*Bull. School of Mines Quarterly*, 1902, xxiii., 348).

To test this idea the following experiments were carried out :—

Experiment V.

A fusion of ore No. 5 was made as in Experiment III. and the melt treated as before, except that the boiling on acidifying was omitted in order to prevent, as much as possible, the formation of the basic iron salts. The solution was heated to the boiling-point and then allowed to cool. The residue still had a brown colour, but it was much lighter than before. The lead was determined by the molybdate method, the percentages found being 61·23 and 61·16.

Experiment VI.

This fusion was also carried out as in Experiment III. The crucible and melt were put into a casserole, and about 75 cc. of water containing 7 cc. of sulphuric acid (sp. gr. 1·84) were added. Enough sulphuric acid was present to neutralise all of the alkali. The melt dissolved in two or three minutes, and the crucible was immediately removed. An excess of 4 cc. of sulphuric acid (sp. gr. 1·40) was then added, and a concentrated solution of sodium bisulphite poured in to reduce the lead peroxide. The solution was boiled for a minute, diluted to 200 cc., cooled, and 20 cc. of 95 per cent alcohol added. The residue was almost pure white. The lead was determined by the molybdate method, 61·46 per cent being found present. On repeating the determination, following the procedure described, the values 61·51 and 61·57 per cent were obtained.

Ore No. 22 was analysed by the same method, 55·89 and 55·88 per cent of lead being obtained. These results agree closely with those obtained by the acid decomposition method. It seems logical to conclude that the low results were due to the presence of the basic salts of iron. The formation of these basic salts may be avoided by dissolving the fusion in acidified water.

In order to determine the value of the above method of decomposition as a general method for the decomposition of other substances containing lead, experiments were carried out in which some typical substances were analysed by the sodium peroxide method, and also by the standard method.

Experiment VII.

A low grade galena ore (No. 45), high in both silica and iron pyrites, was decomposed by boiling with nitric and hydrochloric acids, and the lead determined gravimetrically, 3·13 per cent lead being found. The ore was also decomposed by means of the following charge :—

1·00 grm. ore No. 45 (through 200-mesh sieve) ; 10 grms. sodium peroxide ; 0·8 grm. zinc sulphide ; 0·3 grm. potassium persulphate.

The mixture was ignited by means of a magnesium ribbon. A very hot fusion was obtained, due to the oxidation of the pyrite in the sample. The melt was treated as in Experiment VI. and the lead determined by titration with ammonium molybdate solution, the values 3·16 and 3·19 per cent of lead being obtained in duplicate determinations.

b. Lead Glaze.—A lead glaze high in calcium and silica was analysed by the two methods. A 1 grm. sample of the glaze (200-mesh sieve) was decomposed by the nitric acid method and the lead determined by the molybdate method. The large amount of silica caused difficulties both in filtering the insoluble residue and in dissolving the lead sulphate in ammonium acetate solution, necessitating a much longer boiling.

	1.	2.
Per cent of lead in glaze ..	27·81	27·82

Experiment VIII.

1·0 grm. glaze (200-mesh sieve) ; 10·0 grms. sodium peroxide ; 1·5 grms. zinc sulphide ; 0·4 grm. potassium persulphate.

Since there was no combustible matter in the sample, it was necessary to raise the proportion of zinc sulphide. The fusion was good and the glaze completely decomposed. The melt dissolved in water, the absence of iron making unnecessary the precautions taken in the previous analyses to avoid the precipitation of basic salts. The lead determined by the molybdate method gave 27·84 and 27·82 per cent lead. In this fusion the silica went into solution almost completely and was filtered off from the insoluble residue, and thus did not interfere in the filtering nor in the solution of the lead sulphate.

c. Lead Slag.—A sample of 0·5 grm. of lead slag (100-mesh sieve) was decomposed by nitric and hydrochloric acids and the lead determined by the molybdate method, 36·39 per cent being found.

Experiment IX.

0·5 grm. lead slag (100-mesh sieve) ; 8·0 grms. sodium peroxide ; 1·2 grms. zinc sulphide ; 0·3 grm. potassium persulphate.

Ignited with magnesium wire. The fusion was good and the decomposition appeared to be complete. Since there was very little iron present, the melt was dissolved in water and treated in the usual manner and the lead determined by the molybdate method. Results were 36·58 and 36·48 per cent lead.

These results by the sodium peroxide method compare very favourably with those obtained by the standard nitric and hydrochloric acid decompositions, as may be better seen from Table I.

TABLE I.—*Comparison of Lead Determinations by Standard and by Sodium Peroxide Methods of Decomposition.*

Sample.	Standard method, per cent Pb.	Peroxide method, per cent Pb.
Galena ore No. 5 ..	61·58(*a*)	61·46
,, ,, 5 ..	61·62(*a*)	61·51
,, ,, 5 ..	—	61·57
,, ,, 22 ..	56·04(*a*)	55·89
,, ,, 22 ..	55·98(*a*)	55·90
,, ,, 22 ..	—	55·88
,, ,, 45 ..	3·13(*a*)	3·16
,, ,, 45 ..	—	3·19
Lead glaze	27·81	27·84
,, ...	27·82	27·88
Lead slag	36·39	36·48
,, ...	—	36·58

(*a*) Lead determined gravimetrically as $PbSO_4$.

(To be continued).

A REVISION OF THE ATOMIC WEIGHT OF LEAD.*

PRELIMINARY PAPER.—THE ANALYSIS OF LEAD CHLORIDE.

By GREGORY PAUL BAXTER and JOHN HUNT WILSON.

ALTHOUGH lead is one of the most common elements, its atomic weight has received comparatively little attention, the value at present accepted being based almost wholly upon the work of Stas (see Note).

NOTE.—Earlier work on the atomic weight of lead has been carefully summarised by Clarke, Smithsonian Miscellaneous Collections—Constants of Nature, "A Re-calculation of the Atomic Weights," 1897. In re-calculating the data of earlier determinations the following atomic weights have been used in this paper :—O = 16·000, Ag = 107·88, Cl = 35·46, N = 14·01, S = 32·07. Richards and Wells (*Pub. Car. Inst.*, 1905, No. 28), Richards and Forbes (*Ibid.*, 1907, No. 69, p. 47), Richards and Jones (*Ibid.*, No. 69, p. 69; "Report of International Committee on Atomic Weights," *Journ. Am. Chem. Soc.*, 1907, xxix., 110).

Of the earlier determinations of this constant those of Döbereiner (*Schweig. Journ.*, 1816, xvii., 241) and Longchamps (*Ann. Chim. Phys.*, 1827, xxxiv., 105) can hardly be considered as possessing other than historic interest. The first results which can lay claim to accuracy are those of Berzelius (*Pogg. Ann.*, 1830, xix., 314), who obtained values ranging from 206·7 to 207·3 by reduction of litharge in a current of hydrogen. Berzelius also synthesised the sulphate from metallic lead with the result 207·0 ("Lehrbuch.," Fifth Ed., 1845, iii., 1187). Shortly after, Turner (*Phil. Trans.*, 1833, 527) criticised the first method employed by Berzelius, and attributed the irregularity of his results to the action of lead oxide on the siliceous matter of the tube at the temperature employed in the reduction. By the conversion of both the metal and the oxide into sulphate Turner, in a painstaking research, deduced the values 207·0 and 207·6 respectively, and by converting the nitrate into sulphate, 204·2. Marignac converted metallic lead into the chloride by heating in a stream of chlorine and obtained the result 207·42 (*Ann.*, 1846, lix., 289). Both Marignac (*Journ. Prakt. Chem.*, 1858, lxxiv., 218) and Dumas (*Ann.*, 1860, cxiii., 35) analysed lead chloride. Marignac, who dried the salt at 200°, by titration against silver, found the atomic weight of lead to be 206·81, and from the ratio of lead chloride to silver chloride, 206·85. Dumas subsequently showed that lead chloride, even when dried at 250°, retains moisture and is somewhat basic, and in one analysis in which corrections are applied for these errors, found a somewhat higher value, 207·07, as was to be expected. Chloride analyses by early investigators are, however, to be universally distrusted, owing to neglect of the very considerable solubility of silver chloride, thus producing too low results.

Stas's work upon the syntheses of lead nitrate and sulphate from the metal is undoubtedly the most accurate contribution upon the subject, although a careful consideration of his work discloses minor defects, many of which he recognised himself ("Œuvres Completes," i., 383). The metallic lead used in the syntheses was finally fused under potassium cyanide. Whether or not this treatment introduced impurities into the metal is uncertain. Stas himself suspected the presence of alkalis in the metal. Since the nitrate could not be dried above 150° without decomposition, it undoubtedly contained moisture, and Stas calls attention to this point. The sulphate was made by treatment of lead nitrate, resulting from the nitrate syntheses, with sulphuric acid. The sulphate was dried finally at dull redness, and was probably free, or nearly free, from moisture, although it may have contained traces of lead oxide resulting from occluded nitrate, as well as sulphuric acid. Most of these probable errors tend to lower the observed atomic weight, so that Stas's value from the series of nitrate syntheses, 206·81, and that from the sulphate series, 206·92, are to be regarded as minimum values. The reader of Stas's own account of his work upon lead cannot fail to be impressed with the fact that he was somewhat dissatisfied with the outcome of his research. Mention should also be made of the work of Anderson and Svanberg (*Ann. Chim. Phys.*, 1843, [3], ix., 254) on the conversion of lead nitrate into oxide, although the method was primarily employed in an endeavour to fix the atomic weight of nitrogen. Their results yield the value 207·37.

The discrepancies between the results of these various experiments only serve to emphasise the need of a re-determination of the value in question, and it was with this object in view that the work embodied in this paper was undertaken.

The search for a suitable method for determining the atomic weight of lead failed to reveal any more promising line of attack than those already employed for the purpose. With an element of so high an atomic weight as lead, in any method involving the change of one of its compounds into another, errors which may be insignificant with elements of small atomic weight are magnified in the calculations to undesirable proportions. Furthermore, during the following investigation, reduction of the chloride and oxide in hydrogen was investigated far enough to show that complete reduction of either compound was extremely difficult, if not impossible, without loss of material from the containing vessel by sublimation, aside from the fact that all available material for containing vessels is acted upon by either the fused salt or the reduced metal. The elimination of moisture from lead nitrate or lead sulphate without decomposition of the salts seemed likely to prove a stumbling block in the use of these substances. Finally, in spite of the slight solubility of lead chloride, the determination of the chlorine in this salt by precipitation with silver nitrate was chosen as presenting fewer difficulties. In the first place, the determination of a halogen can be effected with great accuracy. In the second place, the elimination of moisture from lead chloride is an easy matter, since the salt may be fused in a platinum vessel in a current of hydrochloric acid gas without attacking the platinum in the least, and without the production of basic salts. In the third place, silver chloride, which has been

* *Journal of the American Chemical Society*, xxx., No. 2.

precipitated from a dilute solution of lead chloride by means of silver nitrate, does not contain an amount of occluded lead salt large enough to be detected.

Purification of Materials.

Water.—All of the water used in either the purification or the analyses was distilled twice, once from an alkaline permanganate solution and once from very dilute sulphuric acid. Block-tin condensers were used in both distillations, and rubber and cork connections were avoided. Generally, receivers of Jena glass were employed, but in certain cases the water was collected in platinum or quartz vessels.

Hydrochloric Acid.—Commercial C. P. hydrochloric acid was diluted with an equal volume of water and distilled with a quartz condenser, only the middle fraction being collected.

Nitric Acid.—Nitric acid was distilled with a platinum condenser, until free from chlorine. Two distillations were invariably sufficient to accomplish this end, if the first third of each distillate was rejected.

Silver.—Pure silver was obtained by methods already many times employed in the laboratory of Cambridge, Mass. Silver nitrate was dissolved in a large volume of water, and the silver was precipitated as chloride with an excess of hydrochloric acid. The precipitate was thoroughly washed and reduced with alkaline invert sugar. The reduced silver, after being washed, was dried and fused on charcoal in the flame of a clean blast-lamp. After the buttons had been cleaned by scrubbing with sand and etching with nitric acid, they were dissolved in pure dilute nitric acid, and the silver was precipitated as metal with ammonium formate (Richards and Wells, *Pub. Car. Inst.*, 1905, No. 28, 19). This silver was washed and fused in the flame of a blast-lamp on a crucible of the purest lime. The buttons were cleaned as before, and then electrolysed (Abrahall, *Journ. Chem. Soc. Proc.*, 1892, p. 660). Finally, the electrolytic crystals were fused in a boat of the purest lime in a porcelain tube in a current of pure electrolytic hydrogen (Baxter, *Proc. Amer. Acad.*, 1903, xxxix., 249). The bars of silver were cut in pieces with a fine steel saw, etched with dilute nitric acid until free from iron, washed, dried, and heated in a vacuum to 400°. The silver was kept in a desiccator containing solid potassium hydroxide.

Lead Chloride.—Three samples of lead chloride from two entirely different sources were employed. Sample A was prepared from metallic lead. Commercial lead was dissolved in dilute nitric acid, and the solution, after filtration, was precipitated with a slight excess of sulphuric acid. The lead sulphate was thoroughly washed, suspended in water, and hydrogen sulphide was passed in until the sulphate was almost completely converted into sulphide. Next, the sulphide was washed with water, dissolved in hot dilute nitric acid, and the solution was freed from sulphur and unchanged sulphate by filtration. The lead nitrate thus obtained was crystallised twice, dissolved in water, and precipitated in glass vessels with a slight excess of hydrochloric acid. The chloride was washed several times with cold water, and then crystallised from aqueous solution eight times, the last five crystallisations being carried out wholly in platinum, with centrifugal drainage after each crystallisation. In crystallising the lead chloride the whole sample was not dissolved at one time, but the same mother-liquor was used for dissolving several portions of the original salt. Needless to say, the chloride was not exposed to contact with the products of combustion of illuminating gas, lest lead sulphate be formed.

Sample B was prepared from commercial lead nitrate. This salt was dissolved and crystallised from dilute nitric acid, once in glass and six times in platinum vessels, with centrifugal drainage. Hydrochloric acid was then distilled into a large quartz dish, and the solution of the nitrate was slowly added with constant stirring with a quartz rod. The chloride was freed from aqua regia as far as possible by washing with cold water, and was once crystallised from aqueous solution in quartz dishes to remove last traces of aqua regia. Finally, the salt was crystallised three times in platinum.

It could reasonably be expected that both of these samples were of a high degree of purity; nevertheless, upon heating the salt in an atmosphere of hydrochloric acid, the salt itself turned somewhat dark, and upon solution of the fused salt in water a slight dark residue remained. Although in a few preliminary experiments attempts were made to determine this residue by filtration and ignition, it was subsequently found that even a small filter-paper adsorbs appreciable amounts of lead compounds from a solution of the chloride, which cannot be removed by washing with water. From three to thirteen hundredths of a mgrm. of residue were obtained in several blank experiments, by ignition of filters through which ½ per cent solutions of lead chloride had been passed with subsequent very thorough washing. In order to avoid the uncertainty of this correction, further attempts were made to obtain a sample of the salt which would give a perfectly clear solution in water after fusion, and thus render filtration unnecessary. With this end in view a considerable quantity of Sample A was fused in a large platinum boat in a current of hydrochloric acid. The fused salt was powdered in an agate mortar, dissolved in water in a platinum vessel, and the solution was freed from the residue by filtration through a tiny filter in a platinum funnel into a platinum dish, where it was allowed to crystallise. This sample was then twice re-crystallised with centrifugal drainage. Notwithstanding the drastic treatment to which it had been subjected, when a portion of this material was fused in hydrochloric acid, the same darkening as before was observed, and the same residue was obtained. The suspicion that the difficulty was due to dissolving of the filter-paper by the solution of the salt led to a second more successful attempt by crystallisation from hydrochloric acid solution in platinum vessels. (Mr. P. B. Goode, in the laboratory of Cambridge, Mass., has recently found a similar difficulty with the chlorides of the alkaline earths). In this way it was found possible to prepare salt which showed no tendency to darken upon heating, and which, after fusion, left absolutely no residue upon solution in water. Portions of Samples A and B were thus re-crystallised three times more. Since these two specimens of material gave identical results, for two final experiments, portions from each of these samples were mixed and then subjected to three additional crystallisations. This last sample was designated Sample C.

(To be continued).

ON THE DETECTION OF OZONE, NITROGEN PEROXIDE, AND HYDROGEN PEROXIDE IN GAS MIXTURES.

By EDWARD H. KEISER and LeROY McMASTER.

When air is acted upon in a number of ways, such as by electric sparks, the flaming arc, burning hydrogen, burning magnesium, heated platinum wire, &c., in short, by any means which produce very high temperatures, ozone, nitrogen peroxide, and hydrogen peroxide may be formed. The silent electric discharge and the slow oxidation of phosphorus produce oxidising gases in air. Several commercial processes of treating air so as to convert it into a more active chemical agent are at present in use. It is desirable, therefore, to have characteristic reactions for each of the three substances above mentioned in examining the gases produced in these different ways.

A great many reagents have been suggested for this purpose, but many of these have been found to be unreliable, while others are not very sensitive, and still others are rare substances that are not easily obtained. The accompanying table contains a list of such substances, together with a statement of their behaviour toward ozone, nitrogen peroxide, and hydrogen peroxide.

	Ozone.	Nitrogen peroxide.	Hydrogen peroxide.
Potassium iodide and starch (Schönbein, *Ber. u. d. Verh. d. Nat. Ges. Basel*, iv., 58)	Blue.	Blue.	Blue.
Wine-red litmus-paper moistened with potassium iodide (Houzeau, *Ann. Chim. Phys.*, [4], v., 20)	Blue.	No change.	Blue.
Tetramethylparaphenylenediamine (Wurster, *Ber.*, xix., 3195)	Bluish violet.	Bluish violet.	Bluish violet.
Metaphenylenediamine, alkaline solution (Erlwein and Weil, *Ber.*, xxxi., 3158)	Burgundy red or yellow.	No change.	No change.
Manganese chloride paper moistened with guiacum tincture (Engler and Wild, *Ber.*, xxix., 1940)	Blue.	Blue.	No change.
Benzidine in alcohol (Arnold and Mentzel, *Ber.*, xxxv., 1324)	Brown.	Blue.	No change.
Tetramethyl-*pp*-diaminodiphenylmethane in saturated alcoholic solution (Arnold and Mentzel, *Ber.*, xxxv., 1324)	Violet.	Yellow.	No change.
Potassium ferricyanide and ferric chloride (Schönbein, Weltzien, also Schöne, *Ber.*, vii., 1695; Engler and Wild, *Ber.*, xxix., 1940)	No change.	No change.	Blue.
Manganese dioxide or copper oxide (Andrews and Tait, *Liebig's Ann. Chem.*, cxii., 135)	Decomposed.	No change.	Decomposed.
Silver foil (*Ber.*, xxxv., 1326)	Black.	No change.	No change.
Chromic acid and ether (Barreswill, *Ann. Chim. Phys.*, [3], xx., 364)	No change.	No change.	Blue.
Chromic acid (Engler and Wild, *Ber.*, xxix., 1940)	No change.	—	Decomposed.
Titanium hydroxide in sulphuric acid (Schönn, *Zeit. Anal. Chem.*, ix., 41)	No change.	No change.	Yellow.
Thallous salts (Schöne, *Liebig's Ann. Chem.*, cxcvi., 58)	Brown.	No change.	No change.
Ammonium molybdate in sulphuric acid (Schönn, *Zeit. Anal. Chem.*, ix., 41)	No change.	No change.	Yellow.
Guiacum tincture with malt infusion (Struve, *Zeit. Anal. Chem.*, viii., 274)	No change.	No change.	Blue.
Gold chloride free from acid (Böttger, *Zeit. Anal. Chem.*, xix., 105)	Black.	No change.	—
Nitrite test with sulphanilic acid and α-naphthylamine (*Bull. Soc. Chim.*, 1889, [3], ii., 347)	No change.	Pink.	No change.

Arnold and Mentzel have studied a number of the reagents that are mentioned in the preceding list (*Ber.*, xxxv., 1324). They find that potassium iodide and starch, and zinc iodide and starch, as well as guiacum tincture, give a blue colour with ozone, nitrogen peroxide, chlorine, and bromine. In short, these reagents are not characteristic of anything more than an oxidising gas. Red litmus-paper moistened with potassium iodide solution they find to be entirely unreliable, because all paper turns blue with free iodine, and any gas that liberates iodine will turn the paper blue. They also found that a solution of potassium iodide to which wine-red litmus solution had been added was unsatisfactory, because the ozone acts upon the litmus and changes it to a green colour. The third reagent in the above list, tetramethylparaphenylenediamine, is also turned blue by all oxidising gases. Metaphenylenediamine, the fourth one, was unsatisfactory because they found that nitrogen peroxide gave the same colour as ozone, and all oxidising gases give yellowish colours with this substance. Silver foil is not satisfactory because it is not at all sensitive. (Manchot and Kampschulte, *Ber.*, xl., 2891, have recently shown that while silver foil is not at all sensitive at ordinary temperatures, it becomes much more so at 220—240° C.; for metallic mercury they found the temperature at which action was strongest to be 170° C.). Arnold and Mentzel recommend an alcoholic solution of benzidine or, still better, an alcoholic solution of tetramethyl-*p*-*p*-diaminodiphenylmethane. This gives a violet colour with ozone and yellow with nitrogen peroxide; with hydrogen peroxide it remains unchanged. They found, however, that the oxone obtained by the action of sulphuric acid upon barium dioxide had a different action upon this reagent; instead of violet a green colour was obtained. Benzidine, under the same conditions, gave a blue instead of a brown colour. Similar effects were obtained with the ozone from persulphates, percarbonates, and from sodium and hydrogen peroxides.

F. Fischer and Marx (*Ber.*, xxxix., 2555) have used tetramethyl-*p*-*p*-diaminodiphenylmethane or "tetramethyl base," as it is called, in their investigations upon the formation of ozone and nitrogen peroxide in air at high temperatures. They prepared ozone by the silent electric discharge in the Siemens ozonometer, by the action of ultra-violet light, by the electrolysis of sulphuric acid, and in other ways, and found that ozone produces with this reagent a violet colour and the oxides of nitrogen a yellow colour. Mixtures of both gases give a dirty brown colour intermediate between violet and yellow. Another fact that they emphasise is that the paper must always be kept moist; if it becomes dry, ozone changes it to a yellow colour. To detect very small quantities of nitrogen oxides in the presence of ozone they recommend that the gas be conducted into liquid air. The ozone will dissolve while the oxides of nitrogen will separate as blue flakes. When the liquid air is then filtered, the frozen oxides of nitrogen remain upon the filter. The filtrate is allowed to boil, the air distils away, and the ozone remains. In this way both can be separately identified.

This method is open to the objection that liquid air is not readily obtained in many places. Likewise, the "tetra base" of Wurster and the "tetramethyl base" of Arnold and Mentzel are not easily obtainable substances. Moreover, the colour changes are not always satisfactory. Thallous salts and titanic acid are not always at hand. We have now, however, devised a method which is free from these objectionable features and enables us to identify each of these three substances in the presence of the others.

We found that potassium permanganate, even in very dilute solution, is not decolorised by ozone. Nitrogen peroxide and hydrogen peroxide, on the other hand, both reduce it instantly. To identify ozone in gases that contain at the same time nitrogen peroxide and hydrogen peroxide it is only necessary to draw the gases through a solution of potassium permanganate; the nitrogen peroxide and the hydrogen dioxide will not pass through, while the ozone will, and can then be detected with potassium iodide and starch.

To detect nitrogen peroxide in the presence of ozone and hydrogen peroxide we take advantage of the fact that both ozone and hydrogen peroxide are decomposed when passed through a tube containing powdered manganese dioxide. Nitrogen peroxide passes through unchanged. Its presence can be shown by passing the gas, after it has

gone over the manganese dioxide, into very dilute permanganate. If the latter is decolorised, nitrogen peroxide was present. A still more delicate test for nitrogen peroxide is this: pass the gas, which may contain ozone and hydrogen dioxide, directly into pure caustic soda, made from metallic sodium and nitrite-free distilled water, and then test the caustic soda solution for nitrites by the well-known sulphanilic acid and α-naphthylamine method.

Hydrogen dioxide can be identified in the presence of both ozone and nitrogen peroxide by passing the gas mixture into a solution of potassium ferricyanide and ferric chloride. The yellow-brown solution becomes green and then blue as more hydrogen dioxide passes in. This formation of Prussian blue is characteristic of hydrogen dioxide and is not produced by either ozone or nitrogen peroxide. This we have found by experiment.

I. *Examination of the Gases produced by Burning Hydrogen in Air.*

We have tried our method in the examination of the gases produced by burning hydrogen in air. A jet of burning hydrogen was introduced into the end of a glass tube fifteen millimetres in diameter. A current of air was drawn into the tube by means of an aspirator. The gas passed from the tube through a moderately strong solution of potassium permanganate and then into a solution of potassium iodide and starch. This soon became blue, thus showing that ozone was formed by the hydrogen burning in a rapid current of air. The potassium permanganate wash-bottle was then replaced by a tube forty centimetres in length, filled with powdered manganese dioxide. Between this tube and the aspirator, a wash-bottle with a very weak solution of potassium permanganate was inserted. Air was now rapidly drawn through the apparatus and the products of combustion of the hydrogen passed first over the manganese dioxide and then into the dilute permanganate. The latter, after a time, became decolorised, thus showing that nitrogen peroxide was formed. This was confirmed by passing the gases formed by burning hydrogen into a solution of nitrite-free caustic soda and then applying the nitrite test (Griess test) after having slightly acidified the solution. The pink colour was formed, thus confirming the result obtained with dilute permanganate. The gases formed by burning hydrogen were also tested for hydrogen peroxide by drawing them through a solution of potassium ferricyanide and ferric chloride. This became first green, then blue, thus showing that hydrogen peroxide was present. This ferricyanide and ferric chloride test for hydrogen peroxide we found to be more sensitive than titanium dioxide in sulphuric acid. The latter failed to show the presence of hydrogen peroxide in the gases produced by burning hydrogen in air.

II. *Examination of the Gases produced by the Silent Electric Discharge in Air and Oxygen.*

Atmospheric air was purified and dried by being drawn, by means of an aspirator, through a series of wash-bottles containing silver sulphate, potassium permanganate, and pure concentrated sulphuric acid, and was then passed through a Siemens ozonometer. The ozonometer was connected with the terminals of a Ruhmkorff coil, which, in turn, was connected with a storage battery. The potential of the coil discharge terminals was 2160 volts. The air passing through the ozonometer in which the silent discharge was taking place was thereupon conducted through a very weak solution of potassium permanganate. No decolorisation took place, although the ozonised air was passed for more than two hours. Ozone was shown to be present in quantity, not only by its action upon potassium iodide and starch after it had passed through the permanganate, but also by its odour and by the repeated perforation of the rubber tube that connected the last wash-bottle with the aspirator. We were surprised to find that, under these conditions, no nitrogen peroxide was formed. A quantitative determination of the ozone showed that there was 0·00086 grm. per litre. We also conducted the air directly from the ozonometer into pure caustic soda and tested this for nitrites by the Griess test, but failed to obtain any. With potassium ferricyanide and ferric chloride the ozonised air failed to give a reaction for hydrogen peroxide. The same results, namely, the absence of nitrogen peroxide and hydrogen peroxide in air that had passed through the Siemens ozonometer, were obtained when we omitted washing the air with silver sulphate, caustic soda, potassium permanganate, and sulphuric acid before it entered the ozonometer. These experiments show conclusively that it is possible to ozonise air without, at the same time, forming nitrogen peroxide and hydrogen peroxide. We have repeated the above experiments with oxygen, made from fused sodium peroxide and water, instead of air. We obtained no nitrogen peroxide nor hydrogen peroxide. A quantitative determination showed the presence of 0·0012 grm. of ozone to the litre. This ozonised oxygen failed to decolorise potassium permanganate solution.

III. *Examination of Gases produced by the Action of Concentrated Sulphuric Acid upon Barium Dioxide.*

Concentrated sulphuric acid was allowed to drop upon barium dioxide, contained in an Erlenmeyer flask, and the gases resulting were conducted through a concentrated solution of potassium permanganate in a Geissler potash bulb and then into a solution of potassium iodide and starch. A blue colour soon appeared, thus showing the presence of ozone. The gas, after passing over manganese dioxide and then into permanganate, failed to give the reaction for nitrogen peroxide. Nor were we able to detect hydrogen peroxide by passing the gas through a solution of potassium ferricyanide and ferric chloride.

A small quantity of barium nitrate was now added to the barium dioxide, and, on treating with concentrated sulphuric acid and testing as before, we obtained evidence of the presence of ozone and nitrogen peroxide, but not of hydrogen peroxide, in the gases given off.

IV. *Examination of the Gases produced by the Slow Oxidation of Phosphorus in Moist Air.*

We have also used our method for the examination of the gases formed by the slow oxidation of phosphorus in air in the presence of water. We found ozone and nitrogen peroxide but no hydrogen peroxide.

V. *Examination of the Gases produced by the Action of the Flaming Electric Arc upon Air.*

Air that had passed through the flaming electric arc of an Alsop process machine, such as is used in treating flour, was next examined by our method. We found that this air contained nitrogen peroxide, a trace of ozone, and a little hydrogen peroxide.

VI. *Examination of Atmospheric Air.*

We have applied our method to the examination of country air. Air from outside of the laboratory was drawn through a layer of absorbent cotton, six inches in length, then through a concentrated solution of potassium permanganate in a potash bulb, and finally into potassium iodide and starch. After the air had passed through for five hours, a faint blue colour appeared, thus showing the presence of ozone. Air that was filtered through absorbent cotton and that had passed over a layer of manganese dioxide eighteen inches in length was conducted through a very faintly pink solution of permanganate. No decolorisation was observed, although the air was drawn through for eighteen hours. We conclude from this that there was no nitrogen peroxide in the air. Air filtered through cotton was drawn through a solution of potassium ferricyanide and ferric chloride. After four hours the solution acquired a green colour. We found, however, that the reagent used for detecting hydrogen dioxide, namely, a dilute solution of ferric chloride and potassium ferricyanide, when allowed to stand in air, gradually forms a green precipitate,

even when protected from dust by being covered with a bell-jar. We therefore drew atmospheric air for five hours through pure distilled water, contained in a potash bulb, and then tested this water with the reagent. We obtained no blue precipitate, and therefore conclude that the green colour mentioned above may not have been caused by hydrogen dioxide. These experiments prove that our method is sufficiently sensitive to show the presence of ozone in atmospheric air.—*American Chemical Journal*, xxxix., No. 1.

RESEARCHES ON THE DENSITY OF GASES.*

By PHILIPPE A. GUYE.

(Concluded from p. 55).

II. *Discussion of Results.*

Oxygen.—The system of atomic and molecular weights being referred to oxygen (O = 16), the exact determination of the density of this gas is of considerable importance.

Morley (*Zeit. Phys. Chem.*, 1896, xx., 1) has made 41 determinations of this value, of which the averages of three series are :—

Series.	No. of determinations.	Weight of a standard litre.	Capacity of balloon (*a*).
		Grms.	Litres.
I. ..	9	1·42879	21·6 and 8·8
II. (*a*)..	6	1·42887	20·06 ,, 20·56
(*b*)..	9		
III. (*a*)..	7	1·42917	8·83, 16·52 ,, 15·38
(*b*)..	10		

(*a*) Capacities are given in round numbers.

In the first series the temperatures varied between 15° and 20°, measured with mercury and air thermometers, the apparatus being connected with a manometer open to the air. In the second, the balloons were submerged in pounded ice, and the pressure measured by a differential manometer. In the third, the balloons were submerged in ice, the pressure being read on a barometer, the cistern of which communicated with the interior of the balloon.

The oxygen was prepared from potassium chlorate and by electrolysis of a solution of caustic potash for Series III.(*b*). The extreme variations between the individual observations were as follows :—

For Series I. .. .. .. $\frac{4\cdot8}{10{,}000}$

,, II.(*a*) . .. .. $\frac{2}{10{,}000}$

,, II.(*b*) . .. .. $\frac{5\cdot9}{10{,}000}$

,, III.(*a*) . .. .. $\frac{6\cdot8}{10{,}000}$

,, III.(*b*) . .. .. $\frac{7}{10{,}000}$

Referred to the averages, these extreme variations would be reduced to about one-half.

Morley gives double weight to the average of Series III., and thus arrives at the value, 1 litre oxygen = 1·42900 ± 0·000034.

Rayleigh (*Proc. Roy. Soc.*, 1893, liii., 144) used oxygen prepared by three different methods :—(*a*) By heating a mixture of potassium chlorate and sodium chlorate ; (*b*) by heating potassium permanganate ; (*c*) by electrolysis of water, leading the gas thence through a column of copper oxide heated to redness. The balloon was filled at 0° under pressure of about 1 atm. at London, its capacity being 1836·52 cc. The averages of the results (weight of oxygen contained in the calibrated balloon) for each series are :—

Method.	No. of experiments.	Weight of oxygen.	Extreme error.
		Grms.	
Chlorates (*a*) ..	5	2·6269	2·3/10,000
(*b*) ..	5	2·6269	2·3/10,000
Permanganate ..	3	2·6271	1·1/10,000
Electrolysis (*a*) ..	1	2·6271	—
(*b*) ..	2	2·6272	—
Average		2·62704	
Correction for contraction ..		0·00056	
Corrected weight..		2·62760	

One litre of oxygen at Paris = 1·42952.

Dividing the value by 1·00033, the gravity factor, 1 normal litre of oxygen = 1·42905 grms.

Leduc ("Researches sur les Gaz," Paris, 1898), using the balloon method, has reported the density relative to that of air at Paris. He prepared the oxygen (*a*) by electrolysis of an aqueous solution of caustic potash or sulphuric acid, (*b*) by decomposition of potassium permanganate, (*c*) by electrolysis of dilute sulphuric acid, the gas then passing through a column of hot copper oxide.

By the method (*a*) the values, referred to air, varied between 1·10501 and 1·10516, average = 1·1051, extreme variation 1·4/10,000. By the method (*b*), 1·10527 ; by the method (*c*) (3 determinations), 1·10521. (Leduc does not mention the number of determinations ; it would appear that only one was made).

Rejecting the results for (*a*) Leduc adopts 1·10523 for the density of oxygen air referred to at Paris. From this the weight of the normal litre is $\frac{1\cdot29316 \times 1\cdot10523}{1\cdot00033}$ = 1·42876 grms. (taking into account the weight of a litre of air at Paris, determined by the same investigator to be 1·29316, which he claims is accurate to 1/20,000) ; or in round numbers, allowing for the accuracy of 1/20,000 claimed by Leduc, 1 litre of oxygen = 1·4288 grms.

Jaquerod and Pintza (*Comptes Rendus*, 1904, cxxxix., 129), working in this laboratory, have made five determinations of the density of oxygen, obtained by heating potassium permanganate, by filling a volumeter of about 3·5 litres capacity, at 0°, and about 1 atmosphere pressure. These determinations, showing an extreme difference of 6/10,000, give for the weight of the standard litre,—

1 litre oxygen = 1·4292.

These determinations were made by the volumeter method. The authors consider their results to be a little too high, and for their further calculations have adopted the value 1·4290. (D. Berthelot has recently reported all the density determinations made in this laboratory, referred to this unit 1·4292, *Comptes Rendus*, cxliv., 260. In view of the few determinations made, and the reservations made by the authors, this has diminished the accuracy of our other results. In all our other work we have adopted the value 1·4290. See *Journ. Chim. Phys.*, iv., 333).

Gray (*Journ. Chem. Soc.*, 1905, lxxxvii., 1607), in the course of his work on the density of nitric oxide, has made six determinations of the density of oxygen, which show remarkable agreement among themselves. The gas was prepared by heating re-crystallised potassium permanganate. The results give for the weight of a balloon of 267·43 cc. capacity, filled at 0° and 1 atm. pressure at Bonn, the value 0·38228, the extreme variation being only 1·6/10,000. A correction brings the capacity of the balloon to 267·388 cc., so that the weight of a normal litre, taking into account the factor for the gravity at Bonn, is—

1 litre of oxygen = $\frac{0\cdot38228}{0\cdot267388 \times 1\cdot000505}$ = 1·42896 grms.,

a value differing from that of Morley's by only 1/36,000.

* Carried on during 1904, 1905, and 1906 in the Physical Chemistry Laboratory of the University of Geneva. From the *Journal of the American Chemical Society*, xxx., No. 16 ; translated by Helen Isham, from *Archives des Sciences Physiques et Naturelles*, xxiv., 32–62.

Résumé. — Morley's determinations, being the most numerous and carried on under the most varied conditions, would appear to deserve the greatest weight, even though the individual variations are relatively large. Rayleigh's value is 1/20,000 greater than Morley's, while Gray's is 1/36,000 less. On the other hand, the less accurate work of Leduc and Jaquerod and Pintza differ from this by 1/7000, one greater and one less. Whether the mean of all five determinations, or of only the first three, which merit the greater confidence because of the greater number of single determinations and the close agreement between the single determinations, be taken, the value is the same—1·42900. The variations +0·00005 (Rayleigh) and −0·00004 (Gray), from the mean of Morley's values are of the same order as the probable error calculated for the latter (+0·000034).

The value, 1 litre of oxygen = 1·42900, is therefore adopted, and is certainly correct to 1/10,000 and probably to 1/20,000.

Nitric Oxide.—Leduc (*Séances Soc. Franç. Physique*, 1893, p. 214) determined the density of the gas in 1893, and reported it to be 1·0388 referred to air, from which the weight of a normal litre can be calculated to be 1·3429. Leduc suppressed this value in his memoirs published in 1898; therefore it can hardly be taken into account. It is evidently too high. During the investigation carried on with M. Davila we obtained very nearly the same value when using a gas which had not been purified by liquefaction and fractional distillation, so that it would appear that such a high value is due to the presence of traces of nitrous oxide in the gas.

Gray was the first to make an accurate determination of the density of this gas, using the balloon method. The gas was prepared by the action of acetic acid on sodium nitrite and potassium ferrocyanide, washed with caustic potash, dried over phosphorus pentoxide, then liquefied and fractionated at low temperatures. Six determinations, showing an extreme difference of 3/10,000, gave as the weight of the gas contained in the balloon, 0·35851. Six determinations of oxygen (extreme variation 1·3/10,000) gave 0·38228. Adopting Rayleigh's value for oxygen (1·42905) the value for nitric oxide is calculated.

$$1 \text{ litre of nitric oxide} = \frac{1{\cdot}42905 \times 0{\cdot}35851}{0{\cdot}38228} = 1{\cdot}3402 \text{ grms.}$$

On the other hand, he calculates (by private communication), from the capacity of the balloon, 1 litre of nitric oxide = 1·34011 and 1 litre of oxygen = 1·42896. Gray adopts the value 1·3402 grms. This practically conforms with that which would result if the value O_2 = 1·42900 were used.

$$1 \text{ litre NO} = \frac{1{\cdot}4290 \times 0{\cdot}35851}{0{\cdot}38228} = 1{\cdot}34015.$$

Guye and Davila have carried out three series of determinations on gas prepared from three different sources—(*a*) by the action of ferrous sulphate on nitric acid, (*b*) by decomposition by means of mercury of a solution of sodium nitrite acidified with sulphuric acid, (*c*) by the action of sulphuric acid on a concentrated solution of sodium nitrite. The method of purification was in each case the same as that employed by Gray, with the exception that the washing with caustic potash was omitted as it changes a part of the gas to nitrous oxide.

Weighings were made in two balloons of about 0·8 and 0·4 litre capacity, respectively.

Method.	No. of experiments.	Weight of 1 litre.	Extreme error. Large balloons.	Small balloons.
Mercury	6	1·3403	3/10,000	6·7/10,000
Ferrous sulphate .	6	1·3402	3/10,000	4·5/10,000
Sodium nitrite ..	2	1·3401	3/10,000	

The mean of the 14 experiments, together with the mean for each method, gives 1 litre NO = 1·3402, a value identical with Gray's, and which we hereby adopt.

Carbon Dioxide.—Rayleigh reports the density of this gas to be 1·52909 as referred to air. He gives no details as to the method, the number of determinations, or their probable error. The gas was prepared—(*a*) by the action of hydrochloric acid on marble, (*b*) by the same acid on sodium carbonate.

Leduc obtained the mean value of 1·52874 for three very concordant determinations on a gas prepared by the action of hydrochloric acid on marble. He adopts the value 1·5288, in view of the probable error due to traces of air. He also observes that the work of Regnault points to the value 1·5290.

The value for a normal litre can then be deduced as follows:—

1 litre of CO_2 = 1·29284 × 1·52909 = 1·9769 (Rayleigh).
1 litre of CO_2 = 1·29273 × 1·5288 = 1·9763 (Leduc).

Guye and Pintza have determined the weight of a normal litre directly, with a gas generated by heating sodium bicarbonate, and have found 1·9768, the mean of three experiments having an extreme difference of 0·8/10,000. The value finally accepted,—

1 litre of CO_2 = 1·9768,

agrees to about 1/20,000 with Rayleigh's value; it gives a certain weight to the lower result of Leduc, and is justified by a consideration of the probable error. In the course of the work at Geneva, the difficulty experienced in obtaining carbon dioxide entirely free from air has been constantly kept in mind, and the gas which was used in these determinations was entirely soluble in caustic potash.

Nitrous Oxide.—Leduc, Rayleigh, and Guye and Pintza have determined the density of nitrous oxide.

Leduc used the commercial liquefied gas, rectified by distillation (obtained by heating ammonium nitrate). He obtained the densities, referred to air, of 1·5304, 1·5298, 1·5301. Average, 1·5301; extreme error, 3·9/10,000. Rayleigh made his first series of determinations in 1897 with a gas obtained by the decomposition of ammonium nitrate, and purified by dissolving in water—heating to expel the gas, then drying. Five determinations with a probable error of 1·7/10,000, gave the mean value 1·52951 referred to air. In 1904 Rayleigh (*Proc. Roy. Soc.*, lxxiv., A, 181) repeated his work, using the commercial liquefied gas, purified in the same way as above, and obtained practically the same result. He then purified the commercial gas by fractional distillation at the temperature of liquid air, till the density remained constant, and obtained, as the mean of three very concordant observations, with an extreme difference of 0·8/10,000, the value 1·5297.

From this last value of Rayleigh's and from Leduc's, the following values for the weight of the normal litre may be calculated:—

1 litre of N_2O = 1·9780 (Leduc).
1 litre of N_2O = 1·9777 (Rayleigh).

Guye and Pintza have determined the weight of the normal litre directly, using the volumeter method. The gas was prepared by the double decomposition of hydroxylamine sulphate and sodium nitrite. The average of three experiments, having an extreme variation of 2·8/10,000, is—

1 litre of N_2O = 1·9774 (Guye and Pintza).

The impurities which might be found in the commercial nitrous oxide are nitrogen peroxide, air, or nitrogen. The fractionation at low temperatures might not bring about a complete elimination of these impurities, or it might be that the decomposition of hydroxylamine sulphate did not furnish a gas entirely free from air, even though the evacuation of the apparatus was repeated several times. (The washing with alkalis, as practiced commercially, is not sufficient to remove the last traces of NO_2). Under these conditions, and considering the good agreement of the separate determinations made by Rayleigh in 1904, we would adopt for the weight of the normal litre,—

1 litre N_2O = 1·9777 grms.,

which is the mean of the values obtained by Rayleigh, Leduc, Guye and Pintza.

Hydrochloric Acid Gas.—Leduc has determined the density of hydrochloric acid gas, produced by the action of sulphuric acid on sodium chloride, and dried over phosphorus pentoxide, to be 1·2692 as compared with air. There is no indication of the number of determinations or their accuracy, although he considers the last decimal doubtful. A normal litre would be 1·29273 × 1·2692 = 1·6407 grms.

Guye and Gazarian have repeated this determination with a gas prepared in the same way, but further purified by liquefaction at the temperature of liquid air and fractionation at a low temperature (see Note). A preliminary series of four determinations gave a mean of 1·6398, with an extreme variation of 9/10,000.

Note.—These fractionations were for the purpose of eliminating the volatile phosphorus compound, which, according to Richards and Wells (*Journ. Am. Chem. Soc.*, xxvii., 459) is formed when hydrochloric acid passes over phosphorus pentoxide, and which would increase the density of the gas. Our work has also shown that the desiccation of the inside walls of the balloon is accomplished only after repeated rinsings with the hydrochloric acid gas. For these reasons Leduc's value must certainly be a little too high.

Gray, who has undertaken a revision of the density of hydrochloric acid gas, reports a series of six determinations, with a probable error of 3·7/10,000, of which the mean is 1 normal litre = 1·6397. This differs from the preceding by 1/16,000. The mean of these two concordant values would be 1·63975, or, suppressing the last decimal, 1·6398. This value is given only provisionally, until further determinations shall be announced.

Ammonia Gas.—Leduc used ammonia gas obtained from a commercial ammoniacal solution called "pure," which he dried over molten caustic potash. Without reporting the number or the accuracy of his determinations, he gives the value 0·5971 as compared with air, or the weight of 1 normal litre,—

$$1{\cdot}29273 \times 0{\cdot}5971 = 0{\cdot}7719 \text{ grm.}$$

Guye and Pintza have determined the weight of a standard litre, using commercial liquefied ammonia. Assuming that Leduc's high value was due to the presence of organic bases, these experimenters previously purified the gas by leading it over red-hot quicklime, to transform the nitrogen of the organic bases into ammonia. The gas was then collected as ammonium chloride, in this form was recrystallised, and was finally set free by warming the salt with lime, and dried over long columns of recently molten caustic potash. It was entirely soluble in sulphuric acid. Five determinations (using a volumeter of 3·5 litres capacity) with an extreme error of 3·9/10,000 gave a mean value 0·77079, or in round numbers, 1 normal litre = 0·7708. Perman and Davies (*Proc. Roy. Soc.*, 1906, lxxviii., A, 34) have repeated this determination, both by the volumeter method, using a balloon of 1·7783 litres capacity, and by the balloon method, using a balloon of 0·50476 litre capacity. With the gas from a commercial ammoniacal solution, repeating Leduc's procedure, they have arrived at a value 0·7717, almost identical with Leduc's, thus proving the necessity for removing the organic bases. They then purified the gas by three different methods—(*a*) by the method of Guye and Pintza, (*b*) by decomposing with caustic potash, ammonium oxalate which had been ten times re-crystallised, (*c*) by reduction of sodium nitrite, in a caustic soda solution, by aluminium. They obtained the following results :—

Method.	No. of expts.	Weight of 1 litre.	Extreme error.
Volumeter, prepared by *a*, *b*, *c*	7	0·77085	5·2/10,000
Balloon, prepared by *a* ..	4	0·77086	0·8/10,000

The extreme error in the first series is undoubtedly due to the fact of the ammonia gas having been prepared by several methods. The authors advise the value 0·77085.

It appears from these experiments that Leduc's value cannot be considered in deciding upon a final value, as it is unquestionably affected by a constant error due to the presence of organic bases. The mean of the other three values is 1 litre of ammonia = 0·770837, which can be taken in round numbers to be—

$$1 \text{ litre of ammonia} = 0{\cdot}7708,$$

differing from the above by 1/19,000. It takes into account the fact that any source of error (presence of air or of organic bases, traces of moisture or condensation on the surface of the balloon) would tend toward raising the final value rather than lowering it. The mean of the determinations by Perman and Davies, using the volumeter method, which they consider most accurate, and gas prepared by method (*a*), is 0·77080 grm.

(Of the three methods, *a*, *b*, *c*, the first would undoubtedly give the purest gas. The re-crystallisation of ammonium oxalate does not assure a complete elimination of organic bases. which is likewise true of the reduction of sodium nitrite by aluminium, as the latter may contain small amounts of carbon capable of being transformed into organic bases. In the course of my work with Pintza we proved conclusively that the ammonia gas obtained by the decomposition of magnesium nitride contained traces of organic bases. Its density was 1/1935 higher than that of the gas prepared by method *a*).

Sulphur Dioxide.—Leduc reports 2·2639, referred to air, as the mean of several determinations (he does not state the number) having an extreme variation of 1·3/10,000. The gas was prepared by the action of mercury on pure sulphuric acid.

Jaquerod and Pintza, using the volumeter method (capacity of balloon = 3·5 litres) and a gas prepared by repeated fractional distillations of the liquefied sulphur dioxide of commerce, have obtained as the weight of 1 normal litre of sulphur dioxide 2·9266 grms., which represents the mean of seven determinations having an extreme difference of 1·7/10,000.

This result agrees exactly with Leduc's,—

$$1 \text{ litre of sulphur dioxide} = 1{\cdot}29273 \times 2{\cdot}2639 = 2{\cdot}9266.$$

Baume, using two balloons of 0·3 and 0·5 litre capacity, respectively, has recently repeated this determination in the Geneva laboratory and obtained the same result. The gas was purified by the same method as that employed by Jaquerod and Pintza. The extreme variation was 3·8/10,000 for the large and 12·7/10,000 for the small balloon. The mean of the two series is—

$$1 \text{ normal litre} = 2{\cdot}9266.$$

This, therefore, is the accepted value.

Conclusions.

The various results have been tabulated as follows :—In Column I. are the values obtained by Leduc ; in Column II. those obtained by Rayleigh ; in Column III. those of various other investigators (Morley, Ramsay, Gray, Perman and Davies) ; in Column IV. those obtained in the Geneva laboratory ; in Column V. the finally accepted value ; in Column VI., the same value referred to the density of oxygen as 1. This table has been completed by the addition of the better recent determinations of other gases (Dapier, *Journ. Chim. Phys.*, 1907, v., 203, and *Arch. Sci. Phys. Nat.*, [4], xxiv., 34).

The conclusions to be drawn from the work carried on at Geneva during the last three years, compared with that accomplished in other laboratories, are as follows :—

1. The method gives results generally agreeing to at least 1/10,000, when one takes the mean of a half dozen determinations, the extreme difference between any two of which is not more than 3/10,000 or 5/10,000.

2. This agreement may be obtained even with gases as difficultly dried and purified as ammonia, hydrochloric acid, sulphur dioxide, or nitric oxide. For these it is only necessary that the balloon be well dried with dry air, and

Weight of Normal Litre (in Grms.).

Gas.	Leduc.	Rayleigh.	Others.	Laboratory, Guye.	Accepted value.	Referred to density of O_2.
O_2	(1·4288)	1·42905	1·42900 M. 1·42896 Gr.	(1·4292) J. P.	1·42900	1·00000
H_2	0·08982	(0·08998)	0·089873 M.	—	0·08987	0·062890
N_2	1·2503	1·2507	1·2507 Gr.	—	1·2507	0·87523
CO	1·2501	1·2504	—	—	1·2504	0·87502
NO	(1·3429)	—	1·3402 Gr.	1·3402 G. D.	1·3402	0·93786
Ar	—	1·7809	1·7808 R.	—	—	1·2463
CO_2	1·9763	1·9769	—	1·9768 G. P.	1·9768	1·3833
N_2O	1·9780	1·9777	—	1·9774 G. P.	1·9777	1·3840
HCl	(1·6407)	—	1·6397 Gr.	1·6398 G. G.	1·6398	1·1475
NH_3	(0·7719)	—	0·77085 P. D.	0·7708 G. P.	0·7708	0·53940
SO_2	2·9266	—	—	2·9266 J. P. 2·9266 B.	2·9266	2·0480
Air	1·2927	1·2928	—	—	1·2928	0·90469

then rinsed several times in succession with the dry gas which is to be studied. Under these conditions there is no appreciable difference between the mean obtained for a balloon of 3·5 litres capacity and one of 0·5 litre. The surface action is then negligible in work of an accuracy of the order of 1/10,000.

3. The purification of the gas is especially important. The method based on the liquefaction of the gas, followed by distillation at low temperature, is recommended.

4. It is preferable to calculate directly the weight of a litre of the gas under standard conditions, rather than to report the density as compared with that of another gas (oxygen or air). By calibrating the balloon at 0° its volume may be determined to 1/30,000—an accuracy which could be approached, in the density determination, only by a very considerable number of determinations.

5. The most probable values for the density of the gases, determined with an accuracy of the order of 1/10,000, are collected in Columns V. and VI. of the last table.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

Part III.—Analysis of the Aluminium and Iron Groups, including Beryllium, Uranium, Vanadium, Titanium, Zirconium, and Thallium.

By ARTHUR A. NOYES, WILLIAM C. BRAY, and ELLWOOD B. SPEAR.

(Continued from p. 58).

Procedure and Notes (continued).

The Aluminium Group.

Procedure 53.—Acidify the alkaline solution (P. 52) with HNO_3 (1·42), avoiding a large excess; add NH_4OH (0·96) until the mixture after shaking smells of it, and then add 2—3 cc. more. Heat almost to boiling in order to coagulate the precipitate, filter, and wash thoroughly with hot water. (White, flocculent precipitate, presence of *aluminium* (or **beryllium*); colourless solution, absence of *chromium*). (Precipitate, P. 54, or to detect beryllium, *P. 58*g* and *h*; filtrate, P. 55).

Notes.

1. The alkaline solution is acidified with HNO_3, instead of with HCl, because the latter acid might reduce chromic acid, especially if a large quantity were added, or if the acid solution were heated. A moderate excess of NH_4OH must be added in order to keep the zinc in solution, which it does because of the production of $Zn(NH_3)_4{}^{++}(NO_3{}^{-}{}_2)$; but a large excess is to be avoided, since it dissolves $Al(OH)_3$, owing to formation of $NH_4{}^{+}AlO_2{}^{-}$. The zinc is dissolved even when carbonate, phosphate, or oxalate is present.

2. Since aluminium and silica are very likely to be present in the NaOH and Na_2O_2 used as reagents, and since they may be taken up from the dishes, a blank test for these impurities should be made whenever new reagents are employed for the first time, by following P. 52 and 53 and comparing the NH_4OH precipitate with that obtained in any regular analysis. It is also well at the same time to test for zinc by acidifying the NH_4OH solution with acetic acid and following P. 57.

Procedure 54.—Dissolve the precipitate (P. 53), or a small portion of it if it is large, in 5 cc. HNO_3 (1·20). From the appearance of the precipitate estimate the number of milligrms. of aluminium which have been dissolved, and to the solution add about one-fourth as much cobalt as cobalt nitrate, using, however, not less than 0·2 mgrm. Evaporate almost to dryness in a casserole, add a drop or two of water, and soak up the solution in a small piece of filter-paper. Make a small roll of the paper, wind a platinum wire around it to form a spiral, and incinerate the paper in a small flame, finally heating the residue strongly. (Blue residue, presence of *aluminium*).

Notes.

1. This confirmatory test for aluminium should always be tried when the NH_4OH precipitate is small, for general reasons, inasmuch as the precipitation by NH_4OH of an element whose hydroxide is soluble in NaOH is not very characteristic (lead, antimony, tin, and beryllium showing a similar behaviour), but also especially to guard against mistaking SiO_3H_2 for $Al(OH)_3$, for the former substance, if not entirely removed by proper dehydration in the process of the preparation of the solution (in P. 3, Part I.), will appear at this point. A gelatinous precipitate which does not dissolve in HNO_3 indicates silica; it may be tested for by P. 5.

2. The test described in this procedure depends upon the formation of a blue compound, whose formula is not definitely known; but it is doubtless a compound of the two oxides $CoO.xAl_2O_3$, and may be simply cobalt aluminate, $Co(AlO_2)_2$. It may be formed in various ways; but the process described in the procedure seems to be the most suitable one for making the test for aluminium reliable and delicate. It is of the utmost importance to have the aluminium present in excess; for, otherwise, the blue colour is obscured by the black oxide of cobalt. In order that a small enough amount of cobalt may be added, it is convenient to use a very dilute solution of cobalt nitrate, say one that contains one-tenth of a milligrm. of cobalt per cubic centimetre.

3. When the test is properly made, the ash retains the form in which the filter-paper was rolled, and the whole mass, or a large part of it, is coloured blue. The presence of an equivalent amount of phosphate does not spoil the test. When sodium or potassium salts are also present, the ash fuses together, and the test is very unsatisfactory. For this reason the sodium salts present should be all washed out of the NH_4OH precipitate

* From the *Journal of the American Chemical Society*, xxx., No. 4.

before dissolving it in HNO_3. No other element gives a blue colour to the ash, but certain elements, especially iron, obscure the test, so that it can be applied only after other elements have been removed in the regular process of analysis. 0·5 mgrm. Al may be easily detected, and even 0·2 mgrm. after a little practice.

4. Another very good confirmatory test for aluminium consists in dissolving the NH_4OH precipitate in HCl (1·12), adding one and one-half volumes of ether, and saturating the mixture in the cold with HCl gas, as described in *P. 58*g*. Under these conditions aluminium separates in the form of the crystalline compound $AlCl_3.6H_2O$; but no other element of the aluminium group is precipitated, except chromium, which if present in quantity greater than 10—20 mgrms. gives a violet precipitate. Moreover, silica does not interfere with this test. By this process, moreover, beryllium is quantitatively separated from aluminium, and may be tested for in the filtrate.

Procedure 55.—Acidify the NH_4OH solution (P. 53) with 30 per cent acetic acid solution, avoiding an excess of more than 2 cc.

If the solution is colourless, treat it by P. 57.

If it is at all yellow, add about 10 cc. 10 per cent $BaCl_2$ solution, allow the mixture to stand for at least five minutes, and filter. (Yellow precipitate, presence of *chromium*). (Precipitate, P. 56; filtrate, P. 57).

Notes.

1. The presence of less than 0·5 mgrm. chromium as chromate in a volume of 50 cc. makes the solution distinctly yellow, and the addition of $BaCl_2$ is therefore unnecessary when the solution is perfectly colourless. It is to be avoided, since $BaSO_4$ may be precipitated and has then to be removed by filtration. In doubtful cases the colour of the solution should be compared with that of water. The colour test is, of course, not delicate by artificial light.

2. Since some sulphate may be present, the formation of a white precipitate with $BaCl_2$ does not prove the presence of chromium. Whether the precipitate is pure white or yellow should therefore be carefully noted. The yellow colour of a small $BaCrO_4$ precipitate is most apparent when the precipitate has settled or when it has been collected on the filter. If there be sufficient sulphate present to obscure the yellow colour of a little $BaCrO_4$, the confirmatory test for chromium described in the next procedure should be tried.

Procedure 56.—Pour repeatedly through the filter a 5—10 cc. portion of a mixture of 1 volume of HNO_3 (1·20) with 9 volumes of water; to the cold solution in a test-tube add about 2 cc. of ether and 1 cc. 3 per cent H_2O_2, and shake. (Blue coloration of ether layer, presence of *chromium*).

Notes.

1. This blue compound which is formed by the action of H_2O_2 on chromic acid is one of the perchromic acids. It has the formula H_3CrO_7, and appears to be an addition product of H_2O_2 and a higher oxide of chromium. It is a very unstable substance; by its decomposition oxygen is evolved and the chromium is reduced to a chromic salt. Its decomposition is greatly accelerated by an excess of H_2O_2, by the presence of much acid, and by raising the temperature. It is therefore important not to add too much H_2O_2, and to use dilute acid, as directed in the procedure. If, in dissolving the precipitate, the filter be heated with HNO_3, the paper causes the chromate to be reduced to a chromic salt; but when the cold acid is merely poured through the filter this reduction does not take place. If a green solution should be obtained, the chromium must be reoxidised with Na_2O_2 in alkaline solution before making the test. Under proper conditions 0·2 mgrm. Cr may be detected, but the test may fail with a much larger amount if the directions are not followed.

(To be continued).

CORRESPONDENCE.

CONSTITUTION OF THE CARBON MOLECULE.

To the Editor of the Chemical News.

Sir,—I am much interested in Mr. J. C. Thomlinson's suggested geometrical formula for the carbon molecule (Chemical News, xcviii., 37).

As I pointed out in a note appended to a later paper, one factor which would tend to diminish the discrepancy between the experimental and calculated values is the latent heat, for in the first paper (Chemical News, xcvii., 37) I had tacitly assumed that the heat necessary to convert solid carbon into the gaseous state at constant temperature was solely employed in splitting up complex molecules into simpler ones, an assumption which is probably wrong.

With regard to Mr. J. C. Thomlinson's thermal equivalents for the elements, it appears that I have not yet made it quite clear that the data we have at our present state of knowledge relative to the subject reduce to a set of indeterminate equations. It is possible, therefore, by making some assumption to obtain an indefinite number of sets of constants all of which give results in equal agreement with the experimental, so that this forms, in such cases, no criterion of their correctness.

The difficulty is overcome and an unjustifiable assumption avoided by using a set of complex constants, chosen so as to obtain equations which are capable of solution, such as my own system of "fundamental constants."—I am, &c.,

H. Stanley Redgrove.

The Polytechnic, Regent Street, W.

City and Guilds of London Institute.—At a meeting of the Council of the City and Guilds of London Institute held July 27th, it was resolved to award the diploma of "Associate of the City and Guilds of London Institute" to the following matriculated third year students of the Central Technical College who have completed a full course of instruction as prescribed by the Council:—*Civil and Mechanical Engineering*.—F. H. Bramwell (Bramwell Medal), J. C. Gammon, A. Collins, H. A. Jones, W. N. Olliff-Lee, F. H. Rolt, P. H. P. Wells, L. D. Hooper, H. Grinsted, C. A. Bender, R. A. Pook, M. S. Gregory, R. B. Unwin, E. Hudson-Spence, W. E. Woodbridge, H. W. Furlong, E. V. Richards, C. F. Lear, J. B. R. Swan, A. L. Saker, E. F. Matthews, L. F. C. A. Genève, P. M. Chadwick, B. B. Haskew, W. S. Batham, P. P. Husbands, E. Pilditch, O. H. Ripley, C. F. Cleaver, J. G. Porter-Makin, A. M. Low, J. J. A. C. Le Meur, L. G. Scheult, J. O. Archer, J. F. L. Manes, A. E. Jones, H. M. Gorringe, R. D. Morris, R. Engelbach, A. F. Wylie, S. G. Young, G. Avery, R. W. Taylor, A. P. Livingstone-Learmonth, H. A. Joscelyne, J. L. H. J. de Fondaumiere, C. H. Russell, P. A. B. A. Bartlett, O. A. Lindemann, S. D. Ker, T. G. H. Burton, F. N. Forster, C. S. Hawdon, A. C. Selby, H. M. V. O'Brien, A. English, A. H. Masters, E. R. Smith. *Electrical Engineering*.—R. E. Neale (Siemens Memorial Medal and Premium), G. S. Terry, H. E. Poole, F. G. Barrow, R. A. S. Thwaites, L. B. Gilbert, A. H. Finnis, B. A. M. Cooper, E. J. Barnes, D. W. Dye, E. Bate, S. S. A. Watkins, R. J. Spencer-Phillips, R. T. H. Roche, F. W. Geoghegan, E. Holder, J. D. A. Vincent, A. D. Richardson, H. M. Thompson, T. M. Klein, E. A. G. Harvie, M. C. A. H. Genève, C. Kelly, A. F. Henderson, V. W. Newman, J. de la C. Tapia-Contreras. *Chemistry*.—A. R. Runeckles, D. R. Keller, R. C. Gale, W. L. Hodder, L. Marks, S. A. W. Okell, D. R. Pinnock. In addition to the above Certificates have been awarded to twenty matriculated third year students who have completed a full course of instruction at the Central Technical College, and to sixty-two students who have completed a full course of instruction at the Technical College, Finsbury.

THE CHEMICAL NEWS.

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RADIO-ACTIVE CHANGES IN THE EARTH.*

By The Hon. ROBERT JOHN STRUTT, M.A., F.R.S.

You will have already heard during the present Lecture Session from Professor Rutherford, of the recent developments of the new science of radio-activity. I venture to hope, however, that there may be room to say something of aspects of the subject not treated by him. I wish particularly to refer to manifestations of radio-activity which are observed, not in artificially prepared materials like radium, but in the rocks and minerals of the earth's crust, as we find them in nature. Let us consider, in the first place, the most conspicuous cases of this kind. The source from which radium is obtained is the mineral pitchblende. This mineral occurs in veins, like the majority of the useful metals; I may refer particularly to the mineral veins of Cornwall, so long famous as a source of tin. These veins are of the nature of cracks, running through the granite and through the slate which adjoins it. The cracks have been filled up by the various metallic ores which have been introduced by precipitation or sublimation, the exact nature of the process being somewhat obscure.

I will now show you an experiment, due to Sir W. Crookes, which illustrates the radio-activity of pitchblende in a very beautiful manner. A flat polished slab of pitchblende intergrown with a variety of other material which is not radio-active was laid face to face with a photographic plate, which was developed after the lapse of about a week of contact. The radium and other radio-active substances contained in the pitchblende have acted photographically upon the plate, while, of course, those portions of the material which are not radio-active have exerted no such action. Thus pitchblende has, as it were, taken its own portrait, which I now show you on the screen.

Pitchblende, the principal radium ore, contains, as you know, only an infinitesimal percentage of radium, the bulk of the substance being made up of oxide of uranium. Uranium is commonly spoken of as a rare metal; but terms of this kind are comparative only, and in contrast with radium, which is more than a million times scarcer, it seems common enough. Now I wish to speak for a little about this association of uranium and radium in pitchblende. Is it accidental, or has it some special significance? I hope to be able to convince you that it has.

In the early days of radium, it was common to hear the difficulty emphasised, that while there was no reason for doubting that the radium which was found in the earth had been there as long as other metals, a substance that was continually giving out energy in this way was obviously defying the greatest physical generalisation of the Nineteenth Century—the law of the conservation of energy. We cannot, however, afford to sacrifice this law so easily, and a ready mode of escape offers itself, if we suppose that a continual waste of radium is occurring. In that case it becomes necessary to suppose also that the supply is in some way replenished, for otherwise all the radium would have wasted long ago. From what material are the fresh supplies of radium derived? They must be derived from some other substance contained in the mineral where the radium is found, and there is now reason to feel sure that uranium is the substance in question.

We have convincing proof of this, in the fact that the amount of radium found in the mineral is always in direct proportion to the quantity of uranium which it contains. I should perhaps, say, to avoid misconception, that there is good reason for believing that several transitional stages exist through which uranium passes on its road to become radium. It is not necessary, however, to take into account the existence of these intermediate products in order to form a clear idea of the process by which the supply of radium is kept up. Uranium changes spontaneously though very slowly into radium, and the amount of radium produced per annum, for example, will be proportionate to the amount of uranium present. On the other hand, a certain fraction of the total amount of radium present decays per annum, and the balance of this account of profit and loss will represent the amount of radium found in the mineral at any time that we examine it. There will be no difficulty in seeing that on this theory the amount of the radium in the mineral should be proportionate to the amount of uranium, and experiment fully confirms the theory by showing that such is in fact the case. We have here a clear and distinct case of the transmutation of metals, so long unsuccessfully searched for.

Let us now come back to the pitchblende.

What was the source of metalliferous ores found in mineral veins is a very much vexed question, and no solution of it which has yet been proposed can be said to be altogether free from difficulty. One of the most plausible theories, however, supposes that the metals have been derived from the rocks by which the veins are traversed. We are not here concerned with metalliferous ores in general, but only with those which carry radio-active material. In deciding whether the granite of Cornwall can be supposed to furnish the uranium of pitchblende, it is, of course, fundamental to know whether any uranium is present in the rock. It should be said, by way of preface, that the quantity must, at best, be very small, and certainly too small for detection by the methods of chemical analysis as ordinarily applied. We have seen that uranium in nature is invariably accompanied by a proportionate quantity of radium, and as it is in practice much easier to detect minute quantities of radium than to detect the corresponding quantities of uranium, it is best to look for the former only, and to be content to infer the presence of the latter.

I have made a large number of experiments to find out how much radium there may be, not only in Cornish granite, but in a large variety of other rocks. In every case the presence of radium has been established, though only to the extent of about one-millionth part of what is found in pitchblende, and even that, it will be remembered, is not much. If we take into account the very large bulk of the granite and the very small bulk of the pitchblende veins running through it, there is no difficulty in admitting that the granite was capable of supplying the radio-active material of the pitchblende.

Granite, of course, consists of a variety of different minerals, which give it its mottled appearance. These minerals, there is no reason to doubt, have been formed in the successive stages of crystallisation of an originally molten mass. There is a mineral called zircon, of which the jacinths sometimes set by jewellers are a variety, which is present in very minute crystals in granite. These minute crystals of zircon have a very characteristic geometrical shape; a square prism terminated at each end by a pyramid, as you see in the photograph. The fact that they have this perfect shape is a proof that they have been perfectly free to assume their natural form, and have not been hampered for want of space by other minerals surrounding them. The inference is plain that zircon has been one of the first minerals to crystallise in the consolidation of granite.

I have found that this zircon is very much richer in radium than the granite generally, though, on the other hand, it is poor compared with pitchblende. It seems clear that the minerals which crystallise first take an unfair share of the radio-active elements, leaving the rest of the magma impoverished.

In the light of this observation, Professor Joly, of Dublin, has been enabled to explain a curious appearance which is seen when a section of the granite thin enough to

* A Discourse delivered at the Royal Institution, March 27, 1908.

be transparent is examined under the microscope. You see upon the screen one of Professor Joly's photographs of this appearance. This is a minute crystal of zircon, which is imbedded in a large crystal of mica. You will observe that the material surrounding the zircon for a definite distance outwards has become darkened in colour. The altered region round the speck of zircon is practically circular, and is reminiscent of a spot of grease on cloth.

Professor Joly has pointed out that this alteration in the surrounding materials must be due to the radio-activity of the zircon. That radio-active materials are capable of producing such colorations has been known from the early days of radium. You see, for instance, projected on the screen, the image of a glass bottle, in which a radium preparation has been kept. Though originally of colourless glass, it has been stained a deep purple by long continued action of radium.

It may, perhaps, be thought that this idea, though plausible, is no more than a guess. It is, however, much more than that. We know, from the investigations of Professor Bragg and Mr. Kleeman, that the α-particles of radium, which constitute the most important feature of radio-active emission, are only able to penetrate a limited and definite distance into solid materials. They then lose their characteristic properties, if, indeed, they are not altogether stopped. This distance has been measured experimentally, and Professor Joly has shown that the distance is just the same as the distance to which the alteration round the zircon crystals extends. Thus we have full quantitative confirmation of the theory which attributes it to radio-activity.

I will now pass from the discussion of a very minute phenomenon to the discussion of a large scale one. It will be familiar to many of you that, in the opinion of some, at least there is reason for changing the views which have been held for two generations concerning the earth's internal heat. We know that there is, at any rate, some radium in the earth, and that radium gives out heat. Thus it cannot be disputed that some part of the earth's internal heat must be due to this cause; the only question which remains is whether this part is large or small; whether, in fact, the earth's internal heat is chiefly to be accounted for as a small remnant of the much greater internal heat which it once possessed, or whether there is enough radio-active material in the earth to supply most of the annual loss by conduction through the crust and radiation into space.

As I mentioned before, I have made a large number of determinations of the quantity of radium in the rocks of which the superficial portions of the earth are constituted. These are found to be so rich in radium that the difficulty is not so much to account for the internal heat of the earth, as determined by underground observations of temperature, but rather to understand why it is not much hotter. I have suggested, as an explanation, that this general distribution of radio-active material, which pervades the outer parts of the earth, is in reality superficial, extending only to some moderate number of miles in depth, though no doubt much deeper than the deepest mines. I am not wholly satisfied, however, of the sufficiency of this explanation. Radium, and the series of products of which it is one, are not the only radio-active materials in the earth; there is another series, of which thorium is a member, and there is good reason to suppose that thorium is present in rocks in such quantity as to add appreciably to the evolution of heat. Taking this into account, we should probably find, if we had exact data for calculation, that the thickness of rock containing radio-active material was so small that the material of the interior would somewhere have exuded, in the course of the violent dislocations and earth movements which geology reveals to us. No material, however, appears anywhere at the earth's surface which can plausibly be regarded as representative of the unknown interior, if the suggested hypothesis is accepted. It cannot be denied that the subject is at present obscure. Possibly an explanation may be found by supposing that the activity of uranium may be arrested at high temperatures. We have at present no adequate experimental evidence on the subject. It is known that there is very little effect of this kind on radium. If, however, the activity of uranium were arrested at a high temperature, the supply of radium and all the other members of the series would fall off, and thus the aggregate heat production of the whole series might be greatly diminished.

I shall now pass to another branch of the subject. The investigations of Sir William Ramsay and Mr. Soddy have proved that there is continuous evolution of helium from the radium emanation. We have good reasons, into which, however, I do not propose to enter, for considering that the same is true of radio-active changes in general, at all events those in which there is an emission of radiation. Helium is probably evolved at each stage of the transformation of uranium, and at each stage of the transformation of thorium; and it results that the natural minerals and ores in which these elements are found, contain a store of helium, which has accumulated in them, and remains locked up in their pores.

As already mentioned, I have succeeded in determining the presence of radium in granite. Thus it becomes natural to inquire whether the corresponding amount of helium is to be found there too. Nothing of the kind had ever come under observation before, and it was therefore with some interest that I made the experiment. You see before you a vacuum tube of helium prepared from ordinary granite. The characteristic yellow glow will satisfy anyone acquainted with the appearance of a helium discharge of the presence of the gas.

The facility with which helium was detected in granite suggested further experimental problems. The undoubtedly radio-active elements are at present confined to uranium and thorium, and their respective families of descendants. Evidence has been produced, by myself among others, which suggests that lead and some other elements possess a feeble radio-activity of their own. But this evidence is somewhat equivocal. It seemed highly desirable to attack the question in a new way, and the idea suggested itself of looking for helium in the naturally occurring ores of all the elements, common and rare. This had indeed been done, to some extent, from quite a different point of view, by Sir William Ramsay and his coadjutors, in their first investigations on helium; but their observations were directed to finding a practical source of the gas, and were not carried out with anything approaching the minuteness required for the present purpose.

The upshot has been to prove the presence of helium in almost every mineral examined, and even in such unpromising materials as rock crystal, or common quartz sand. The quantity found in the various cases has varied very widely. In fact, minerals may be found having any helium content, from thorianite, which contains 10 cc. per grm., down to rock crystal, which contains about a ten-millionth part of that quantity.

I have here a small tube of helium obtained from clear, colourless rock crystal, and you will have no difficulty in seeing the characteristic yellow glow as before.

Are we to regard the helium in common minerals as due to a feeble radio-activity of the common elements? No doubt such an hypothesis is tempting, but it must be rejected. Radium is present everywhere in traces, and these traces are in general sufficient to account for the minute quantities of helium. This is illustrated in the table below, which gives in round numbers the actual amount of helium extracted from various minerals by heat, and the amount of helium reckoned relatively to the radium.

There is reason to think, as already mentioned, that the presence of thorium would constitute another source of helium. But it is believed that this complication does not produce any appreciable effect in these cases. You will see that minerals like quartz, though they contain actually only an infinitesimal quantity of either substance, still show about the same proportion of helium to radium as the

Mineral.	Helium present, c.mm. per kil.	Helium ratio, *i.e.*, ratio of helium to radium (arbitrary scale).
Normal—		
Samarskite	1,500,000	14
Hæmatite	700	9
Galena	2	17
Quartz	2	10
Abnormal—		
Beryl	33,000	954

minerals which are rich in both. We may conclude that helium is connected with radium in the poor minerals as in the rich ones.

I have, however, encountered an interesting exception to this rule in the mineral beryl. Beryl is, in all essentials, the same as emerald; the latter name is kept for stones which are of a clear deep green colour, but scientifically the distinction is of no importance. Some beryls contain enormously more helium than can be accounted for by the small traces of radium in them. Nor do they contain any appreciable quantity of other radio-active material. What view, then, can we take of the presence of helium in this mineral? It is, to me at least, difficult to believe that the gas can have been introduced from without. If not, can it have been generated from radium formerly existing in the beryl, but now exhausted? This, too, seems unlikely, for it would imply that beryls are older than other minerals, and there is no plausibility in such a theory from the geological standpoint. My own opinion is that, in all probability, an element hitherto unknown exists in the mineral, from which the helium is generated. It may be objected that, in that case, the mineral ought to be radio-active. If, however, the radiation were emitted with less than the critical velocity, we should not be able to detect it, and nothing is known to make such an hypothesis improbable.

In conclusion, I shall be well content if I have convinced you that there is still something to be learnt from careful examination of the most commonplace materials. If there is nothing new under the sun, there are, at least, unsuspected things going on inside the earth, where the sun cannot penetrate.

CHEMICAL PUBLICATIONS IN AMERICA IN RELATION TO CHEMICAL INDUSTRY.*

By W. A. NOYES.

The American Chemical Society holds a unique place among the chemical societies of the world. It combines functions and activities which could heretofore be found only in separate organisations. It is the only large chemical society in the world which includes both those who are engaged in the application of chemistry to the industries and to chemical engineering, and those who are engaged in teaching and in researches with no immediate practical bearing, and which provides adequately for the interests of all classes of chemists. There are two reasons which justify this policy. In these days of intense specialisation one of the greatest dangers to a professional man is that he will become so intensely absorbed in the field in which he is working that he loses all interest in other lines of work, and falls out of touch with the rapid advances which his science is making in every direction. This tendency is almost as marked and fully as dangerous for those who are engaged in pure research as for those working in applied chemistry. Both classes of our members find that contact with chemists having a radically different point of view is exceedingly stimulating and useful. The advantages of an abstract journal which covers both fields are so self-evident as scarcely to require remark.

* An Address delivered at the New Haven Meeting of the American Chemical Society, July 2, 1908.

The second reason, which justifies the union of all classes of chemists in a single society, is that only in this way is it possible to provide at moderate expense those publications which are needed by every chemist. The chemists of the world seem to have realised only very dimly the advantages in economy which result from combination for purposes of publication. The fundamental principle is that for a small circulation the original cost of gathering the material and setting the type forms a large proportion of the total cost of publication. After the matter has once been accumulated and printed, the cost of printing and distributing additional copies is relatively small.

The German Chemical Society, when it began to publish officially the *Chemisches Zentralblatt*, adopted the plan that the journal was to be sent only to those who will pay for it. The result is that those who take the *Zentralblatt* must pay 9 dols. a year for it, in addition to the dues of the Society, and the journal goes to about one-half of the members. The total circulation of the *Zentralblatt* is only about 2000. The American Chemical Society in establishing *Chemical Abstracts* has adopted a different plan. While it was recognised that a few of our members might not care for the journal, it was seen that by increasing the dues of all the members, it could be sent to all at a comparatively moderate expense. Accordingly the dues were increased by 3 dols. for all members. While *Chemical Abstracts* costs, at present, between 5 and 6 dols. per member, it is securing such support among the chemists of America and of the world that the permanent success of the enterprise seems to be assured. In adopting the budget for 1907, the Council considered that if enough new members were gained during the first year to make up for those who fell out on account of the increase of dues we should do well. Instead of that the Society had a net gain of 310 members. When *Chemical Abstracts* was started in January, 1907, we had a membership of 3079. We now have 3800 members.

In establishing *Chemical Abstracts* it was recognised that the funds available would not permit of the publication of as large a journal as the *Chemisches Zentralblatt*. It has, however, approached much more nearly to the size of that journal than was anticipated, and while the abstracts in some divisions are relatively brief, it may be fairly said that *Chemical Abstracts* covers the whole field of chemistry better than any other similar publication. To illustrate, *Chemical Abstracts* gives abstracts of American, English, German, and French patents, while the *Zentralblatt* gives abstracts of German patents only. The number of abstracts in biological, mineralogical, and geological chemistry greatly exceeds the number in the same lines in the *Zentralblatt*, and the same is true of all lines of technical chemistry. The total number of abstracts, even in the first year of publication, is also greater in *Chemical Abstracts*, although the total number of pages is less.

The fields covered by *Chemical Abstracts* are so varied that at the low subscription price of 6 dols. a year it should secure many subscribers among persons whose primary interest is in other sciences than chemistry. Physicians and biologists will find much that is of value to them under biological and pharmaceutical chemistry; physicists will be interested in physical chemistry, radio-activity, and electro-chemistry; and geologists in mineralogical and geological chemistry.

As an almost necessary result of what has been stated about publication, the American Chemical Society has accepted the principle that it can afford to extend the benefits of its membership to anyone who is willing to pay the dues. The statement has recently been made that this has resulted in a membership which is largely non-professional. Such a statement is wholly misleading. While the fact that a man is a member of the Society is no guarantee that he is a trained chemist, there are very few members who are not engaged in chemical work, and I think I am safe in saying that 90 per cent of the members have had a good chemical training.

The American Chemical Society is about to establish a

Journal of Industrial and Engineering Chemistry. This journal, too, is to be sent to all members of the Society. The objection has been raised that it should be sent only to those members who are especially interested in it. Such a course does not seem wise for two reasons. First, in accordance with the ideal of the Society, which is to care adequately for the needs of all classes of chemists, we wish to continue to furnish all of our members with original papers as well as with abstracts in all fields of chemistry. Second, if we were to adopt the other plan, we could afford to give as a rebate to anyone who does not care for the journal only the amount which would be saved by printing a smaller number of copies. This amount is so small as to be scarcely an object. We seem to be justified, therefore, in adopting for the Industrial Journal the same plan which has met with so much success in the case of *Chemical Abstracts*.

The broad policies which have been adopted by our Society can succeed only on the basis of a very large membership. We need the loyal support of every American chemist. We are also securing support from nearly every civilised country in the world—from England, Germany, South Africa, Australia, New Zealand, China, Japan, Chili, Brazil, Argentina, and many others.

THE DECOMPOSITION OF CERTAIN MINERALS AND INDUSTRIAL PRODUCTS BY MEANS OF SODIUM PEROXIDE AND METALLIC SULPHIDES.*

By JAMES H. WALTON, Jun., and HERMAN A. SCHOLZ.

(Concluded from p. 64).

Sodium Peroxide Method of Decomposition applied to Manganese Determinations.

SINCE the sodium peroxide and zinc sulphide mixtures were so effective as fluxes in the lead determinations, they were tried on manganese compound.

a. Analysis of Manganese Glaze.—A manganese glaze high in silica, but containing no calcium, was first used. It was not attacked to any appreciable extent by nitric and hydrochloric acids, even after boiling for an hour. One grm. of the glaze (200-mesh sieve) was fused with sodium carbonate in a platinum crucible. The melt was dissolved, made acid with sulphuric acid (sp. gr. 1·42), and the manganese determined by Volhard's method (*Ann. Chem. Liebig*, cxcviii., 318).

	1.	2.
Per cent of MnO in the sample ..	4·57	4·55

Experiment X.

1·0 grm. manganese glaze (200-mesh sieve); 1·4 grms. zinc sulphide; 1·0 grm. sodium peroxide; 0·4 grm. potassium persulphate.

Ignited in a nickel crucible by means of magnesium ribbon. Very good fusion and apparently complete decomposition, for no residue was left on acidifying with sulphuric acid and adding a little sodium sulphite. The melt was dissolved in water, acidified with sulphuric acid (sp. gr. 1·42), and sodium bisulphite was added to reduce manganese dioxide. The sulphur dioxide was boiled off and the manganese determined by Volhard's method. Results: 4·57 and 4·55 per cent MnO.

b. Analysis of Franklinite.—The sample of franklinite contained considerable silica. As is well known, it is a very refractory mineral which cannot easily be decomposed by sodium carbonate fusion, is decomposed with great difficulty by potassium bisulphate fusion, and is decomposed by concentrated nitric and hydrochloric acids only after long boiling. A 1 grm. sample (200-mesh sieve) was boiled for two hours with nitric acid (sp. gr. 1·42) containing a small quantity of hydrochloric acid (sp. gr. 1·12). Ten cc. sulphuric acid were added and the solution boiled down to sulphuric acid fumes. It was diluted and the manganese determined by Volhard's method. Results were: 7·89 and 7·96 per cent MnO.

Experiment XI.

1·0 grm. franklinite (200-mesh sieve); 8·0 grms. sodium peroxide; 1·2 grms. zinc sulphide; 0·4 grm. potassium persulphate.

Ignited by magnesium in a nickel crucible. The mixture became liquid and red-hot, but the decomposition was not complete. The proportions of the components were varied, but it was impossible to get a complete decomposition with these ingredients. It was therefore decided to substitute for the zinc sulphide some substance which would give more heat. Iron pyrites and a small amount of magnesium powder were found to answer this requirement very well.

Experiment XII.

1·0 grm. franklinite (200-mesh sieve); 8·0 grms. sodium peroxide; 0·3 grm. powdered magnesium; 0·3 grm. potassium persulphate; 2·0 grms. pyrites.

Ignited by magnesium wire in a nickel crucible. The fused mass was extremely hot and remained liquid and red-hot for about two minutes. It gave a complete decomposition of the franklinite, but the melt dissolved very slowly, in about two hours. This was remedied by sifting 3 to 4 grms. of sodium peroxide into the liquid mass and gently rotating the crucible to mix the peroxide with the molten mass. The contents of the crucible, after cooling, dissolved easily in water in three to four minutes. The solution was made acid with sulphuric acid (sp. gr. 1·42), the manganese dioxide reduced by sodium bisulphite, and the manganese determined by Volhard's method as in the other determination.

	1.	2.
Percentage of MnO ..	7·90	7·88

c. Analysis of Ferro-manganese.—A 0·5 grm. sample of ferro-manganese which had been passed through a 100-mesh sieve was dissolved by boiling for about an hour in nitric acid (sp. gr. 1·42). Sulphuric acid was added and the solution was evaporated to sulphuric acid fumes. The manganese was determined by Volhard's method as in the franklinite determinations. Results were 56·25 and 56·23 per cent manganese.

Experiment XIII.

0·5 grm. ferro-manganese (100-mesh sieve); 8·0 grms. sodium peroxide; 0·8 grm. zinc sulphate; 0·3 grm. potassium persulphate.

Ignited by means of magnesium ribbon. A red-hot liquid mass was obtained, and the substance apparently decomposed completely. The melt dissolved with difficulty. Three to four grms. of sodium peroxide sprinkled into the fused mass produced a melt that was dissolved easily in a few minutes. The solution was acidified with sulphuric acid, the manganese dioxide reduced with sodium bisulphite, and the manganese determined by Volhard's method as before. Results: 56·18 and 56·32 per cent manganese.

TABLE II.—*Comparison of Standard and Sodium Peroxide Methods of Decomposition for Manganese Determinations.*

Sample.	Standard method, per cent MnO.	Peroxide method, per cent MnO.
Manganese glaze ..	4·57	4·58
„ „ ..	4·55	4·55
Franklinite	7·89	7·90
„	7·96	7·88
	Per cent Mn.	Per cent Mn.
Ferro-manganese ..	56·25	56·18
„ ..	56·23	56·32

The manganese in each case was determined by Volhard's method.

* *American Chemical Journal*, xxxix., No. 7.

The Decomposition of Chrome-Iron Ore.

For these experiments a chrome-iron ore high in chromium was used. It was first analysed by fusing in a porcelain crucible with sodium peroxide, dissolving the fused mass in water, and destroying the excess of the peroxide by boiling. To the dichromate solution an excess of standard ferrous sulphate solution was added, and the excess above that necessary to reduce the sodium dichromate was determined by titrating with standard potassium dichromate. The results obtained were 47·09 and 47·12 per cent Cr_2O_3.

Experiments with a charge similar to that used in Experiment XI. showed that not enough heat is obtained with the zinc sulphide to completely decompose the chrome-iron ore. A mixture of pyrite and magnesium was found o work satisfactorily.

Experiment XIV.

0·5 grm. chrome-iron ore (through 200-mesh sieve); 8·0 grms. sodium peroxide; 0·3 grm. potassium persulphate; 2·0 grms. iron pyrites; 0·3 grm. magnesium.

Ignited in the usual manner. The fusion was very hot, but it was necessary to sift 3—4 grms. of sodium peroxide in the liquid mass to make it dissolve easily. The chromium was determined volumetrically, 47·07 per cent being found in the sample.

The Application of the Sodium Peroxide Method of Decomposition to Silica Determinations.

In order to investigate the adaptability of the sodium peroxide method to silica determinations, a blast-furnace slag was decomposed by this method and by the standard method and the percentages of silica obtained by the two methods compared. For the standard method 1·0 grm. of the slag (200-mesh sieve) was boiled for an hour with hydrochloric acid (sp. gr. 1·12). The slag appeared to be completely decomposed. It was evaporated to dryness on the water-bath and kept there for several hours after it was dry. It was moistened with hydrochloric acid, dissolved in water, and the silica filtered off. The filtrate was dehydrated a second time. The silica was ignited to constant weight in a platinum crucible and then volatilised in the usual manner, the silica being determined by difference. The results obtained were 30·06 and 30·04 per cent SiO_2.

Experiment XV.

0·5 grm. slag (200-mesh sieve); 8·0 grms. sodium peroxide; 1·2 grms. zinc sulphide; 0·3 grm. potassium persulphate.

Ignited the above mixture by means of magnesium ribbon in a nickel crucible. A good fusion was obtained. The melt dissolved easily in water and no residue was left on acidifying with hydrochloric acid. The silica was dehydrated twice and determined as before. The results were 30·02 and 29·98, as against 30·04 and 30·06 per cent by the standard method.

Qualitative Experiments.

Qualitative experiments were carried out in order to test the adaptability of this method to the decomposition of various substances.

a. Monazite.—The sodium peroxide method of fusion was tried on a sample of monazite containing 2·75 per cent ThO_2.

Experiment XVI.

1·0 grm. monazite (200-mesh sieve); 8·0 grms. sodium peroxide; 1·2 grms. zinc sulphide; 0·3 grm. potassium persulphate.

Ignited the above mixture with magnesium ribbon. The decomposition was complete, for upon acidifying with hydrochloric acid no residue was left.

b. Clays.—A brick-clay of the following composition was used:—SiO_2, 60·93; Al_2O_3, 17·93; Fe_2O_3, 8·12; MgO, 0·91; CaO, 1·35; Na_2O and K_2O, 5·01; volatile matter, 5·73 per cent. (This analysis and the one of the fire-clay were made by the chemists of the Illinois State Geological Survey).

Experiment XVII.

1·0 grm. clay (200-mesh sieve); 8·0 grms. sodium peroxide; 1·2 grms. zinc sulphide; 0·3 grm. potassium persulphate.

It was ignited by means of a magnesium ribbon. The fusion was quiet. The fused mass dissolved completely in hydrochloric acid, leaving no residue.

Experiments were made with a fire-clay of the following composition:—SiO_2, 67·37; Al_2O_3, 21·69; Fe_2O_3, 1·59; TiO_2, 1·32; loss on ignition, 8·70 per cent.

Experiment XVIII.

1·0 grm. fire-clay (200-mesh sieve); 8·0 grms. sodium peroxide; 0·3 grm. potassium persulphate; 1·2 grms. zinc sulphide.

The above mixture was ignited by means of magnesium ribbon. The melt, when taken up in water and made acid with hydrochloric acid, went into solution completely, leaving no insoluble residue. This method may be used advantageously in connection with the determination of titanium by the method described by one of the authors (Walton, "The Colorimetric Determination of Titanium," *Journ. Am. Chem. Soc.*, 1907, xxix., 481).

c. Copper Matte.—A copper matte high in copper was used in the following experiments:—

Experiment XIX.

1·0 grm. copper matte (200-mesh sieve); 8·0 grms. sodium peroxide; 0·5 grm. zinc sulphide; 0·3 grm. potassium persulphate.

This mixture was ignited in the usual manner. The mass became very hot and liquid. It was necessary to sift 3 to 4 grms. of sodium peroxide into the molten mass to make it dissolve easily. The melt, when taken up in water and acidified with hydrochloric acid, dissolved completely, leaving no residue.

d. Bauxite.—A sample of bauxite containing a considerable amount of iron and titanium oxides was used for the following experiments:—

Experiment XX.

0·5 grm. bauxite (200-mesh sieve); 8·0 grms. sodium peroxide; 1·2 grms. zinc sulphide; 0·3 grm. potassium persulphate.

Ignited by means of magnesium ribbon. The fusion was good, but the decomposition of the ore very poor. Consequently the pyrite mixture was tried.

Experiment XXI.

0·5 grm. bauxite; 8·0 grms. sodium peroxide; 0·5 grm. zinc sulphide; 1·0 grm. pyrites.

Ignited the above mixture by means of a magnesium ribbon. The fusion was extremely hot. Three or four grms. of sodium peroxide were sifted into it to make the melt dissolve easily. The melt was dissolved in water acidified with hydrochloric acid. No residue was left, which indicated complete decomposition.

e. Titanium Iron Ore.—For a titanium iron ore, high in iron and titanium, a mixture essentially the same as that used in Experiment XX. was used, but it did not decompose 0·5 grm. of the ore (200-mesh sieve).

A fusion of a mixture similar to that used in Experiment XXI. completely decomposed 0·5 grm. of the ore.

Notes and Precautions.

To ascertain the effect of the fusions on the nickel crucibles, two new crucibles were weighed, and after sixteen fusions had been made in each they were carefully cleaned and weighed again. The crucible weighing originally 18·7683 grms. lost 0·2876 grm. in sixteen fusions. A crucible weighing originally 18·6119 grms. lost 0·3363 grm. in sixteen fusions. This is an average loss

in weight of about 0·02 grm. for each fusion. When the hot oxidising nature of the fusions is considered, this is a very slight loss. The fusions were those made with the lead ores, using sodium peroxide and zinc sulphide.

It was found that a piece of twine about an inch long, soaked in alcohol and lighted, can be used for igniting the mixtures instead of magnesium ribbon. This could be used if, for any reason, magnesium was not to be introduced into the mixture.

A finely divided sample was found to be necessary for the sodium peroxide fusions. In the foregoing experiments, with the exception of the ferro-manganese and the lead slag, it was found necessary to pass the substance to be analysed through a 200-mesh sieve.

Since sodium peroxide often contains small lumps which keep the mixture from igniting or cause incomplete combustion, it is necessary to pulverise this substance before using it.

The different ingredients must be very thoroughly mixed. A partial mixing results in partial decomposition.

All the ingredients *must be perfectly dry*. The mixture is so easily ignited that if there is any moisture present it may react with the sodium peroxide and evolve enough heat to ignite the mixture prematurely.

Conclusion.

From the foregoing experiments it is evident that sodium peroxide, zinc sulphide, and potassium persulphate, when mixed in certain proportions, give a good fusion medium for the decomposition of the substances used in this investigation. In every case the new method gave results as good as those obtained by the standard method. With possibly slight modifications, it could be extended to numerous other substances, a few of which are indicated in the qualitative experiments. This method is particularly applicable to sulphide ores and to substances high in silica, such as glazes and slags. With basic substances, such as franklinite and chrome-iron ore, it is necessary to use iron pyrites to get sufficient heat. Pyrite, however, cannot be used in a good many fusions where iron is objectionable, and to fusions of that nature this method cannot be applied.

The chief advantage of the method is the quickness with which decomposition can be accomplished. The entire operation, including mixing, igniting, cooling, and dissolving the melt, takes approximately five minutes. A decomposition by acid takes from half an hour to an hour and a half or even two hours. Moreover, in most cases the nitric or hydrochloric acid must be expelled by evaporating the solution down to sulphuric acid fumes, which necessitates considerable care and usually takes half an hour longer. In the sodium peroxide method sulphuric acid may be used directly for acidifying, which does away with the tedious evaporation.

In the new method the silica present is practically all brought into solution and kept there, so that it does not clog filters and cause other annoyances. The sulphur in sulphide ores and the carbonaceous matter in slags, &c., is easily and completely oxidised by the sodium peroxide method, and the laborious oxidation by means of nitric acid is avoided.

Another advantage arises from the fact that since these fusions are made in nickel crucibles, a saving is made in the amount of platinum ware used.

Magnetic Oxides of Chromium.—Ivan Shukoff.—The decomposition of chromic acid gives a mixture of different oxides, one at least of which can exist in two states, one strongly and the other very feebly magnetic. To determine the precise composition of the magnetic oxide measurements were taken of the specific magnetism of different magnetic oxides of variable composition, to find for which composition the magnetic properties were most highly developed. Thus the formula of the magnetic oxide was found to be $2CrO_3.Cr_2O_3$.—*C. R.*, cxlvi., No. 26.

A REVISION OF THE ATOMIC WEIGHT OF LEAD.*

PRELIMINARY PAPER.—THE ANALYSIS OF LEAD CHLORIDE.

By GREGORY PAUL BAXTER and JOHN HUNT WILSON.

(Concluded from p. 65).

Method of Analysis.

THE lead chloride contained in a weighed platinum boat was first fused in a current of pure dry hydrochloric acid gas. This gas was generated by dropping concentrated sulphuric acid into concentrated hydrochloric acid, and after being washed with a saturated solution of hydrochloric acid, was passed through five towers filled with beads moistened with freshly boiled concentrated sulphuric acid to dry the gas. It has already been shown that phosphorus pentoxide may not be used for this purpose (Baxter and Hines, *Journ. Am. Chem. Soc.*, 1906, xxviii., 779). After the salt had cooled, the hydrochloric acid was displaced by dry nitrogen, and this in turn by dry air. Nitrogen was prepared by passing air charged with ammonia over red-hot rolls of copper gauze, the excess of ammonia being removed by means of dilute sulphuric acid. The gas was passed over beads moistened with a dilute silver nitrate solution and over solid caustic potash to remove sulphur compounds and carbon dioxide respectively, and was finally dried by concentrated sulphuric acid and phosphorus pentoxide. The air was purified and dried in a similar fashion. The apparatus for generating the hydrochloric acid and for purifying the hydrochloric acid and nitrogen was constructed wholly of glass with ground-glass joints. The platinum boat containing the fused chloride was next transferred to a weighing bottle without exposure to moist air, by means of the bottling apparatus, which has frequently served for a similar purpose in many atomic weight investigations in the Chemical Laboratory of Harvard College (Richards and Parker, *Proc. Am. Acad. Arts and Science*, 1896, xxxii., 59). After standing some time in a desiccator in the balance room, the weighing bottle was weighed. In most of the analyses the lead chloride was dissolved from the boat by prolonged contact with boiling water in a Jena glass flask. In the last two analyses, in order to show that no error was introduced through solubility of the glass, the solution was prepared in a large platinum retort, and was not transferred to the precipitating flask until cold.

Very nearly the necessary amount of pure silver was then weighed out and dissolved in a re-distilled nitric acid diluted with an equal volume of water in a flask provided with a column of bulbs to prevent loss by spattering. After the silver was all dissolved, an equal volume of water was added, and the nitrous fumes were expelled by gentle heating. The solution was then further diluted until not stronger than 1 per cent, and added slowly, with constant agitation, to the solution of lead chloride contained in the precipitating flask. The precipitation and handling of the silver chloride were conducted in a room lighted with ruby light. The flask was shaken for some time and allowed to stand for a few days, with occasional agitation, until the supernatant liquid had become clear. Thirty cubic centimetre portions of the solution were then removed and tested with hundredth normal silver nitrate and sodium chloride, in a nephelometer (Richards and Wells, *Am. Chem. Journ.*, 1904, xxxi., 235; 1906, xxxv., 510), for excess of either chloride or silver, and, if necessary, standard silver nitrate or sodium chloride was added, and the process of shaking and testing repeated until the amounts of silver and chloride were equivalent. The test solutions were always returned to the flask, since they contained appreciable amounts of silver chloride, and the weight of silver chloride subsequently obtained was corrected for the quantity thus introduced. Furthermore, if an excess of silver was found, a negative correction of an equivalent quantity of silver chloride was necessary.

* *Journal of the American Chemical Society*, xxx., No. 2.

The Atomic Weight of Lead.

Series I.—$PbCl_2 : 2Ag$.

No. of analysis.	Sample of $PbCl_2$.	Weight of $PbCl_2$ in vacuum.	Weight of Ag in vacuum.	Weight of Ag added or subtracted.	Corrected weight of Ag.	Atomic weight of Pb. Ag = 107·930, Cl = 35·473.	Atomic weight of Pb. Ag = 107·880, Cl = 35·457.
		Grms.	Grms.	Grms.	Grms.		
1.	A	4·67691	3·63061	−0·00074	3·62987	207·179	207·079
2.	A	3·67705	2·85375	—	2·85375	207·189	207·089
3.	A	4·14110	3·21388	+0·00020	3·21408	207·173	207·073
4.	A	4·56988	3·54672	—	3·54672	207·185	207·085
5.	B	5·12287	3·97596	−0·00028	3·97568	207·201	207·101
6.	B	3·85844	2·99456	—	2·99456	207·186	207·086
7.	B	4·67244	3·62628	—	3·62628	207·189	207·089
8.	C	3·10317	2·40837	—	2·40837	207·188	207·088
9.	C	4·29613	3·33427	−0·00020	3·33407	207·202	207·102
	Average..					207·188	207·088

Series II.—$PbCl_2 : 2AgCl$.

No. of analysis.	Sample of $PbCl_2$.	Weight of $PbCl_2$ in vacuum.	Weight of AgCl in vacuum.	Loss on fusion.	Weight of asbestos.	Weight AgCl from wash-waters.	Corrected weight of AgCl.	Atomic weight of Pb. Ag = 107·930, Cl = 35·473.	Atomic weight of Pb. Ag = 107·880, Cl = 35·457.
		Grms.	Grms.	Grm.	Grm.	Grm.	Grm.		
10.	A	4·67691	4·82148	0·00100	0·00021	0·00204	4·82273	207·188	207·088
11.	A	4·14110	4·26848	0·00020	0·00008	0·00180	4·27016	207·192	207·092
12.	B	5·12287	5·28116	0·00054	0·00013	0·00197	5·28272	207·181	207·081
13.	B	3·85844	3·97759	0·00035	0·00033	0·00192	3·97949	207·136	207·036
14.	C	3·10317	3·19751	0·00045	0·00014	0·00189	3·19909	207·261	207·161
15.	C	4·29613	4·42730	0·00020	0·00004	0·00268	4·42982	207·204	207·104
	Average							207·193	207·093
	Average, rejecting the least satisfactory analyses (13 and 14) ..							207·191	207·091
	Average of Series I. and II.							207·190	207·090

After the exact end-point had been obtained, about two-tenths of a grm. of silver nitrate in excess was added in order to precipitate the dissolved silver chloride, and the flask was thoroughly shaken, and allowed to stand again until the solution was perfectly clear. The silver chloride was washed, first several times with a very dilute silver nitrate solution containing four hundredths of a grm. per litre, and then eight times with pure water. It was next transferred to a Gooch crucible and dried for several hours in an electric oven, the temperature being gradually raised to 180°, and was cooled in a desiccator and weighed. In every case the moisture retained by the precipitate was determined by fusion in a small porcelain crucible. The silver chloride, dissolved in the filtrate and washings, was determined by comparison with standard solutions in the nephelometer in the usual manner. Care was taken to treat both tubes in exactly the same manner, and final readings were taken only when the ratio had become constant. Before proceeding to the nephelometer tests, however, the filtrate and washings were passed through a very small filter in order to collect a small quantity of asbestos shreds mechanically detached from the Gooch crucible. The filter was ignited and weighed, the ash being treated with a drop of nitric and hydrochloric acids in order to convert any reduced silver into chloride. In order to find out whether lead or silver nitrates were appreciably adsorbed by the filter-paper, a solution containing lead nitrate, silver nitrate, and nitric acid of the concentration of these filtrates, was passed through several small filter-papers, which were then very carefully washed. In four cases, after incineration of the papers, there was found, −0·00001, +0·00002, +0·00003, +0·00001 grm. of residue, exclusive of ash. This correction is so small that it is neglected in the calculations. In all the analyses the platinum boat behaved admirably, the loss in weight never amounting to more than a few hundredths of a milligrm.

The balance used was a short arm Troemner, easily sensitive to a fiftieth of a milligrm. The gold-plated brass weights were carefully standardised to hundredths of a milligrm. All the weighings were made by substitution with tare vessels as nearly like those to be weighed as possible.

Vacuum corrections: The values of the density of lead chloride as given by various observers range from 5·78 to to 5·805 (Landolt-Börnstein-Meyerhoffer, "Tabellen"), the mean of the more accurate determinations being 5·80. This gives rise to a vacuum correction of +0·000062 for each apparent grm. of lead chloride, the density of the weights being assumed to be 8·3. The other vacuum corrections applied were silver chloride +0·000071, and silver − 0·000031.

All analyses which were carried to a successful completion are recorded in the tables.

The close agreement of the averages of the two series is strong evidence that no constant error, such as occlusion, affects the results. Furthermore, in all, 19·55663 grms. of silver produced 25·98401 grms. of silver chloride, whence the ratio of silver to silver chloride is 132·865, a value in close agreement with the result 132·867 obtained by Richards and Wells (*loc. cit.*). The different samples, A, B, and C, all give essentially identical results.

It appears, then, that if the atomic weight of silver is taken as 107·93 (O = 16·000), the atomic weight of lead is 207·19, nearly three-tenths of a unit higher than the value now in use. If the atomic weight of silver is 107·88, a value probably nearer the truth than 107·93, lead becomes 207·09, a number still much higher than that depending upon Stas's synthesis, as is to be expected.

We are greatly indebted to the Carnegie Institution of Washington for assistance in pursuing this investigation, also to Dr. Wolcott Gibbs and to the Cyrus M. Warren Fund for Research in Harvard University for many indispensable platinum vessels.

Ergosterin and Fungisterin.—C. Tanret. — Ergosterin in ergot of rye is accompanied by a similar crystalline substance called by the author fungisterin, which appears to be present in other fungi. The two substances may be separated by a method based upon the difference between their solubilities in ether, ergosterin being the less soluble. The two substances occur in many different families of cryptogams, and apparently Gérard's generalisation is correct, viz., that all the cholesterins existing in the lower forms of plant life belong to the ergosterin group.—*Comptes Rendus*, cxlvii., No. 1.

ON THE CALCULATION OF THERMO-CHEMICAL CONSTANTS.

V.—THE CALCULATION OF THE THERMAL CONSTANTS OF AROMATIC SUBSTANCES.

By H. STANLEY REDGROVE, B.Sc. (Lond.), F.C.S.

IF we attempt to calculate the thermal constants of aromatic substances, we are beset by the difficulty of the constitution of benzene; such formulæ as those of Kekulé, Ladenburg, &c., giving inaccurate results (CHEMICAL NEWS, xcv., 301). It would be useful therefore to adopt some means of calculation, in which the question of the constitution of benzene is not introduced, where the primary object is to find out whether various groups exhibit the same thermal behaviour in aromatic as in aliphatic compounds.

This can be readily done by referring such compounds back to benzene, using the constants ζ = the molecular heat of combustion of benzene, as determined by experiment (and corrected for constant volume), and ζ' = the corresponding molecular heat of formation of benzene; whence ζ = 797·9 cals. and ζ' = −13·7 cals. (Thomsen).

This method we have already employed in calculating the fundamental thermal constants for oxygen compounds (CHEMICAL NEWS, xcvii., 253 *et seq.*); we now apply it to the other aromatic compounds, whose heats of combustion have been determined by Thomsen, not containing groups or atoms whose thermal behaviour we have not yet investigated; these compounds are three hydrocarbons and phenyl chloride.

Using the above method the molecular heats of combustion and formation of these substances have been calculated, and are exhibited, together with the differences between them and the experimental, and the percentage errors (in the case of the molecular heats of combustion) in Table I. The two oxygen compounds already considered are also given for the sake of completeness.

The agreement in all cases is perfectly satisfactory, showing that the various groups exhibit the same thermal behaviour in aromatic as in aliphatic compounds.

To facilitate reference we give in Table II. a list of the constants employed in this paper, with their respective values, together with references to the CHEMICAL NEWS wherein the method of calculating them and their respective significations will be found.

TABLE I.—*Aromatic Compounds.*

		Molecular heats of combustion.					Molecular heats of formation.			
1. Substance.	2. Formula.	3. Formula.	4. M.H.C. (Thomsen) constant volume. Cals.	5. M.H.C. calc. Cals.	6. Diff. between cols. 4 and 5. Cals.	7. Error. Per cent.	8. Formula.	9. M.H.F. (Thomsen) constant volume. Cals.	10. M.H.F. calc. Cals.	11. Diff. between cols. 9 and 10. Cals.
Toluene	$C_6H_5.CH_3$	$\zeta+\alpha-\beta$	953·9	956·2	+2·3	+0·24	$\zeta'+\alpha'-\beta'$	−5·3	−7·5	−2·2
Mesitylene ..	$C_6H_3(CH_3)_3$	$\zeta+3\alpha-3\beta$	1280·0	1272·8	−7·2	−0·56	$\zeta'+3\alpha'-3\beta'$	−2·4	+4·9	+7·3
Pseudocumene.	$C_6H_3(CH_3)_3$	$\zeta+3\alpha-3\beta$	1279·2	1272·8	−6·4	−0·50	$\zeta'+3\alpha'-3\beta'$	−1·6	+4·9	+6·5
Phenyl chloride	$C_6H_5.Cl$	$\zeta-\chi$	762·9	762·4	−0·5	−0·07	$\zeta'-\chi'$	−12·4	−12·0	+0·4
Anisol	$C_6H_5.O.CH_3$	$\zeta+\alpha-\omega$	934·8	933·3	−1·5	−0·16	$\zeta'+\alpha'-\omega'$	+13·8	+15·3	+1·5
Phenol	$C_6H_5.OH$	$\zeta-\omega_1$	767·6	768·2	+0·6	+0·08	$\zeta'-\omega_1'$	16·6	16·0	−0·6

TABLE II.

M.H.C. constant. Cals.	Reference.	M.H.F. constant. Cals.	Reference.
α = 210·8	xcv., 301	α' = 21·2	xcvi., 188
β = 52·5	do.	β' = 15·0	do.
χ = 35·5	xcvii., 183	χ' = −1·7	xcvii., 185
ω = 75·4	xcvii., 253	ω' = −7·8	xcvii., 253
ω_1 = 29·7	xcvii., 255	ω_1' = −29·7	xcvii., 255

The Polytechnic, Regent Street, W.

THE ESTIMATION OF IRON AND VANADIUM IN THE PRESENCE OF ONE ANOTHER.

By GRAHAM EDGAR.

THE difficulties in the separation of vanadic acid from iron were early recognised. In 1877 Bettendorf (Poggendorff's *Ann. der Phys.*, clx., 126) noted that ammonium hydroxide precipitates from a solution containing these substances a yellow vanadate of iron not entirely decomposed by an excess of the reagent. He therefore added an excess of ammonium phosphate and boiled the solution, whereby the iron was converted into ferric phosphate and precipitated as such on the addition of ammonium hydroxide, while the vanadium remained in solution. Carnot (CHEM. NEWS, lvi., 16) used repeated precipitation by ammonium hydroxide, ammonium acetate, or ammonium sulphide, this process serving to remove iron but not aluminium or chromium. According to Classen (*Am. Chem. Journ.*, vii., 349), vanadic acid may be separated from iron in ores by fusion with sodium carbonate and sodium nitrate, and extraction of the melt with water, the vanadium going into solution as sodium vanadate. According to Arnold (*Electrochemist and Metallurgist*, March-April, 1902), in the analysis of steel, a fusion of sodium peroxide and extraction with water serves to obtain the vanadic acid in solution, free from iron. Fritcherle (CHEM. NEWS, lxxxii., 258), in the analysis of carnotite, precipitated iron together with uranium and vanadium with an excess of sodium carbonate, then added sodium hydroxide and boiled for some time, the vanadic acid alone going into solution. Blum (*Zeit. Anal. Chem.*, xxxix., 156), in separating vanadium from rather large amounts of iron, as in pig-iron, states that the separation is only complete when, after precipitation of the iron as hydroxide or basic acetate, the precipitate is re-dissolved, tartaric acid added, and the iron precipitated by means of an excess of ammonium sulphide, the solution being allowed to stand for several hours. Campagne (*Ber.*, xxxvi., 3164) separates the greater part of the iron in ferrovanadium and vanadium steel by repeated extraction of the hydrochloric acid solution with ether, afterward determining the vanadium by repeated evaporation with concentrated hydrochloric acid, removal of this acid by means of sulphuric acid, and titration with potassium permanganate. He states that if it be desired to determine the iron present, the original solution, without extracting with ether, may be boiled repeatedly with hydrochloric acid to reduce the vanadic acid, the hydrochloric acid removed by means of sulphuric, and the vanadium titrated with permanganate. If then the solution be reduced with hydrogen sulphide, the excess of gas removed by boiling, and the solution again titrated with permanganate, the difference between the two titrations will give the iron present. Glasmann (*Journ. Russ. Phys. Chem. Ges.*, xxxvi., 77) effects the separation by adding potassium iodide to the sulphuric acid solution, removing the free iodine by means of sulphur dioxide, neutralising

Ferric alum in receiver (10 per cent).	$KMnO_4$, N/10×9545.		V_2O_5.			Fe_2O_3.		
	I.	II.	Taken.	Found.	Error.	Taken.	Found.	Error.
Cc.	Cc.	Cc.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
35	31·90	58·02	0·1136	0·1137	+0·0001	0·1437	0·1436	- 0·0001
35	31·90	58·04	0·1136	0·1138	+0·0002	0·1437	0·1435	- 0·0002
35	31·85	58·00	0·1136	0·1138	+0·0002	0·1437	0·1433	- 0·0004
35	31·90	58·00	0·1136	0·1136	—	0·1437	0·1437	—
20	25·30	38·35	0·0568	0·0568	—	0·1437	0·1423	−0·0004
20	25·29	38·30	0·0568	0·0566	- 0·0002	0·1437	0·1433	0·0004
20	15·98	29·02	0·0568	0·0568	—	0·0719	0·0721	+ 0·0002
50	38·50	77·60	0·1704	0·1702	−0·0002	0·1437	0·1442	+0·0005
50	38·45	77·60	0·1704	0·1704	—	0·1437	0·1438	+ 0·0001
50	38·45	77·58	0·1704	0·1703	−0·0001	0·1437	0·1439	+0·0002
35	22·50	48·60	0·1136	0·1136	—	0·0719	0·0720	+ 0·0001
35	22·50	48·60	0·1136	0·1136	—	0·0719	0·0720	+ 0·0001
35	22·45	48·58	0·1136	0·1137	+0·0001	0·0719	0·0716	- 0·0003
20	15·97	29·07	0·0568	0·0570	+0·0002	0·0719	0·0718	- 0·0001

with potassium hydroxide, and precipitating the iron by means of a mixture of potassium iodide and iodate. The liberated iodine is removed by sodium thiosulphate, the ferric hydroxide filtered off, and the vanadium estimated in the filtrate.

Among other methods of separation may be mentioned that of Classen (*Ber.*, xiv., 2771), who precipitates the iron electrolytically from a solution of the double oxalates, and Myers (*Journ. Am. Chem. Soc.*, xxvi., 1124), who deposits the iron, using a mercury cathode, the vanadium in both cases remaining in solution.

In view of the difficulties attendant upon the separation of iron and vanadium, and in view of the increasing importance of such substances as ferrovanadium and vanadate of iron, composed almost entirely of these elements, it has been thought advisable to present a method by which vanadium and iron may be estimated in the presence of each other.

If a solution containing vanadic acid and iron be reduced by means of sulphur dioxide, the reoxidation by potassium permanganate proceeds according to the equation—

$$5V_2O_4 + 10FeO + 4KMnO_4 = 5V_2O_5 + 5Fe_2O_3 + 2K_2O + 4MnO \quad (1).$$

If this solution, after titration, be passed through a column of amalgamated zinc in the Jones reductor, the receiving flask being charged with a solution of ferric sulphate, the reduction is carried, in the case of vanadic acid, to the condition of V_2O_2 (Gooch and Edgar, *Am. Journ. Sci.*, xxv., 233), and the re-oxidation by permanganate proceeds according to the equation—

$$5V_2O_2 + 10FeO + 8KMnO = 5V_2O_5 + 5Fe_2O_3 + 4K_2O + 8MnO \quad (2).$$

The difference in the number of cubic centimetres of permanganate used in the first and second titrations is evidently used in oxidising the vanadium from the condition of V_2O_2 to V_2O_4, and multiplied by the factor 0·00456 (for exactly N/10 solutions), gives the amount of vanadic acid present. This being known, the iron present may be calculated from the amount of permanganate used in either titration.

In the experiments in Table I. three standard solutions were used, viz. :—

1. A solution of potassium vanadate, slightly acidified with sulphuric acid, and containing 11·36 grms. of vanadic acid to the litre. This solution was standardised by the method of Holverscheit (Inaugural Dissertation, Berlin, 1890).

2. A solution of ferric alum, slightly acid, with sulphuric acid and containing 14·37 grms. of ferric oxide to the litre. This solution was standardised by the very accurate method of Newton (*Am. Journ. Sci.*, xxv., 343).

3. An approximately tenth normal solution of potassium permanganate (3·16 grms. per litre), standardised against a N/10 solution of arsenious oxide.

The details of manipulation were as follows :—Measured portions of the ferric sulphate solution were mixed with portions of the solution of vanadic acid, and a current of sulphur dioxide was passed through the slightly acid mixture until the colour had changed from red into green, and finally into a clear blue. A few centimetres of dilute sulphuric acid were then added, and the solution heated to boiling, the current of sulphur dioxide being replaced by one of air-free carbon dioxide. When the last traces of sulphur dioxide had been removed, the flask was cooled in running water, the atmosphere of carbon dioxide being maintained, and when thoroughly cool, titrated with potassium permanganate until the colour had changed from blue into yellowish green. The solution was then heated to 70—80° and the titration completed at that temperature. The solution, having now a volume of 100—150 cc., was passed through a column of amalgamated zinc in a long Jones reductor, being preceded by 150 cc. of hot dilute (2½ per cent) sulphuric acid and followed by 100 cc. of dilute acid and finally 200 cc. of distilled water. The receiving flask, containing an excess of ferric sulphate, was kept cool by means of running water, and its contents, after the addition of syrupy phosphoric acid to remove the colour of the iron, were titrated with permanganate until the colour had changed from bluish green to yellow, and the colour of the permanganate began to be persistent and destroyed only by shaking. The flask was then heated to 70—80° and the titration completed in the hot solution.

The results given in the table show that iron and vanadium may be readily estimated in the presence of each other by two oxidations with potassium permanganate, following reduction first with sulphur dioxide and last with amalgamated zinc, under the conditions described above.

In conclusion, the author desires to thank Prof. F. A. Gooch for advice given in the course of the work.—*American Journal of Science*, xxvi., July, 1908.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

PART III.—ANALYSIS OF THE ALUMINIUM AND IRON GROUPS, INCLUDING BERYLLIUM, URANIUM, VANADIUM, TITANIUM, ZIRCONIUM, AND THALLIUM.

By ARTHUR A. NOYES, WILLIAM C. BRAY, and ELLWOOD B. SPEAR.

(Continued from p. 72).

Procedure 57.—Warm the acetic acid solution (P. 55 or *P. 58*f*) to 50° or 60°, saturate it in a small flask with H_2S, cork the flask, and allow it to stand for five or ten minutes if no precipitate separates at once. (White flocculent precipitate, presence of *zinc*). Filter through a double filter (two filters folded together), wash once with a little water. Reject the filtrate.

* From the *Journal of the American Chemical Society*, xxx., No. 4.

To confirm the presence of zinc, pour a 5—10 cc. portion of HNO_3 (1·20) two or three times through the filter containing the H_2S precipitate. To the solution add an amount of cobalt as cobalt nitrate equal to about one-fourth of the amount of zinc estimated to be present, using, however, not less than 0·2 mgrm. cobalt. Evaporate in a casserole almost to dryness to expel the acid, neutralise with 10 per cent Na_2CO_3 solution, and add about 0·5 cc. in excess. Evaporate to dryness, ignite gently until the purple colour due to the cobalt disappears, and allow the casserole to cool. (Green colour, presence of *zinc*).

Notes.

1. ZnS precipitates more rapidly, and in a somewhat more flocculent form, from a warm solution. Very small quantities of zinc (less than 1 mgrm.) may be missed unless a short time be allowed for the precipitate to coagulate; but, since sulphur may then separate, the appearance of a white turbidity is not sufficient proof of the presence of zinc. The precipitate may be allowed to settle, in order that the amount of zinc present may be better estimated. A double filter is used, since the ZnS is apt to pass through the filter.

2. The immediate formation of a white flocculent precipitate with H_2S in acetic acid solution is so characteristic as to be a sufficient test for zinc. Manganese is the only other element of this group that forms a light coloured sulphide; and this, owing to its greater solubility in water, does not precipitate from an acetic acid solution. The confirmatory test described in the last paragraph of the procedure is, however, useful when only a small non-coagulating precipitate, which may be sulphur, results, or when, owing to the presence of a small quantity of other elements, the precipitate is dark coloured.

3. The green compound obtained in the confirmatory test is doubtless a compound of cobalt and zinc oxides, perhaps cobalt zincate, $CoZnO_2$. The conditions under which the zinc and aluminium compounds of cobalt are formed are very different. As we have seen, the aluminium compound is formed only at very high temperatures, and the test is not at all delicate in the presence of a salt of an akali element. On the other hand, the zinc compound is obtained at comparatively low temperatures, and the presence of an alkali is essential. Excess of cobalt must, of course, be avoided, for the black cobalt oxide completely obscures the green colour. A larger proportion of cobalt than is recommended in the procedure may be added without danger, but the test is very satisfactory even when a large excess of zinc is present.

**Procedure* 58*a*.—To the filtrate from the Na_2O_2 precipitate (P. 52), add HNO_3 (1·20), keeping the solution cool, until it reacts slightly acid and any precipitate just re-dissolves upon shaking. (See Note 1). Dilute the solution to 100 cc. and transfer it to a strong 200 cc. bottle. Add solid $NaHCO_3$, a little at a time, until the mixture after shaking no longer turns blue litmus-paper red at once; finally add 1·0—1·5 grms. solid $NaHCO_3$ (weighed out roughly). Close the bottle with a tightly fitting cork, wire it in, wrap a cloth around the bottle, place it in a vessel of warm water, and boil the water gently for twenty or thirty minutes. Cool the bottle to at least 50° (best by slowly adding cold water to the bath), remove the cork, filter at once, and wash, using suction if the precipitate is large. Filtrate, *P 58*b*; precipitate, *P. 58*f*).

Notes.

1. If up to this point in the analysis there has been no indication of any of the elements that are to be tested for in the alkaline solution, time may often be saved by determining before treating with $NaHCO_3$ whether any of them are present by proceeding as follows:—To one-fourth of the solution, which has been acidified with HNO_3, add NH_4OH (0·96) in small excess, note whether a precipitate forms, and then add a few drops of $(NH_4)_2S$ solution. Even if there is no precipitate, vanadium may be present; to test for this, add 3 cc. NH_4OH (0·90) and completely saturate with H_2S (see *P. 51*a*). If the results of these tests show that any of these elements are present, treat the remainder of the HNO_3 solution by the regular procedure. If, on the other hand, the results are negative, no further treatment is necessary.

2. The alkaline solution is kept cold during the neutralisation and an excess of HNO_3 is avoided because chromate in the presence of H_2O_2 and an acid is rapidly reduced to a chromic salt, especially when the solution is hot. This reduction, if complete, would prevent the detection of chromium in the subsequent test. H_2O_2 will, to be sure, not be present, since Na_2O_2 is very rapidly destroyed by the boiling of the alkaline solution in P. 52, except when uranium is also present; in this case the peruranate which is formed by the treatment with Na_2O_2 is not decomposed upon boiling, but breaks up into a uranyl salt and H_2O_2 upon acidification.

3. The success of this separation depends upon securing the proper concentration of the $NaHCO_3$. Since the $NaHCO_3$ may be at first used up in precipitating zinc, aluminium, and beryllium as well as in neutralising the free acid, the weighed amount of $NaHCO_3$ is added only after the solution ceases to react distinctly acid. A much larger concentration of $NaHCO_3$ than 1·0 to 1·5 per cent would not prevent the complete precipitation of zinc or of aluminium, but it would interfere with that of beryllium. Thus with a volume of 100 cc. the precipitation of the beryllium is complete when the concentration of the $NaHCO_3$ is 1 per cent., and 1 mgrm. can usually be detected when it is 2 per cent, but 3 mgrms. remain dissolved in a 3 per cent solution, about 15 mgrms. in a 5 per cent solution, and about 150 mgrms. in a 10 per cent solution. A smaller concentration of $NaHCO_3$ and a smaller volume than 100 cc. are avoided, in order to prevent as far as possible the precipitation of uranyl vanadate, which may otherwise occur when large quantities of uranium and vanadium (about 100 mgrms. of each) are simultaneously present. The presence of phosphate or oxalate (or chromate) does not cause the precipitation of uranium, nor otherwise interfere with the analysis. When only small amounts of the elements of this group are present, the separation can be made in a smaller volume, care being taken that the concentration of the $NaHCO_3$ rather than the quantity taken be that prescribed.

4. If it is desired, the separation may be made in an open flask; but in this case the solution must not be boiled and the $NaHCO_3$ solution should not be stronger than 1 per cent. The process is then best carried out by digesting the mixture on a water-bath for twenty to thirty minutes in a flask covered with a watch-glass. Under these conditions neither zinc nor beryllium dissolve in significant quantity; but 1 to 2 mgrms. of aluminium may be completely dissolved. The mixture must not be boiled, for a larger amount of aluminium may then dissolve (as much as 5 mgrms. on one minute's boiling).

5. When a large amount of aluminium or beryllium is present, 2 to 5 mgrms. of uranium may be carried down almost completely in the $NaHCO_3$ precipitate, so that in this case uranium has to be tested for in the analysis of the precipitate.

6. In a dilute solution of $Na^+HCO_3^-$ saturated with CO_2, the hydrogen ion and hydroxyl ion concentrations are both very small and are nearly the same as in pure water. AlO_3H_3, basic $BeCO_3$, and $ZnCO_3$ are completely precipitated because the solubility of these substances is not much increased through removal of the OH^- or $CO_3^=$ by combination with H^+ with formation of H_2O or HCO_3^- (leaving the cations Al^{+++}, Be^{++}, or Zn^{++} in the solution) or through removal of the metal ions by combination with the OH^- with the formation of AlO_2^-, $BeO_2^=$, or $ZnO_2^=$. The higher hydroxides

of chromium and vanadium (chromic and vanadic acids) are soluble polybasic acids, which are so much more highly ionised than H_2CO_3 that they displace it from its salt $NaHCO_3$, forming mainly sodium hydrogen chromate or vanadate. The fact that uranium is not precipitated, even though $Na_2U_2O_7$ is difficultly soluble, may be due to the formation of a complex sodium uranyl carbonate.

(To be continued).

CORRESPONDENCE.

THE THERMO-CHEMICAL RELATIONS OF CARBON, HYDROGEN, AND OXYGEN.

To the Editor of the Chemical News.

Sir,—With reference to my letter to the Chemical News (vol. xcviii., p. 46) I have reconsidered the foundations of any theory of themo-chemical equivalence.

Any difficulty in notation which must occur when symbols currently in use are altered in any way whatsoever leads me to point out that, in my earlier paper (Chemical News, xciii., 37), I state that carbon has a divalent function in acetylene. This would, as the context shows, indicate that carbon in carbon monoxide has the same heat value as one carbon atom in unsaturated hydrocarbons where there is an unsaturated carbon valency represented by two bonds.

With this reservation I append the accompanying table for unsaturated hydrocarbons.

	Heat of formation (cals.).	
	Experiment.	Calculated.
Propylene	3·220	4·090
Tri-methylene ..	−3·470	−4·080
Isobutylene	10·660	10·600
Allylene	−39·950	−42·370
Di-propargyl ..	−96·040	−97·780

—I am, &c.,

J. C. Thomlinson.

6, Villa View, Low Fell, Gateshead,
August 4th, 1908.

CONSUMPTION OF SODIUM NITRATE.

To the Editor of the Chemical News.

Sir,—Will Dr. Franks kindly explain the data in the Chemical News, vol. xcvii., p. 289, how it is possible that Europe absorbs only about 340,000 tons of sodium nitrate, while Germany alone imports over 500,000 tons yearly?—I am, &c.,

Dr. A. Batez.

Plzen, Bohemia.

NOTICES OF BOOKS.

Catalogue of Lewis's Medical and Scientific Circulating Library. New Edition, revised to the end of 1907. London: H. K. Lewis. 1908.

The catalogue of this circulating library shows that the volumes it comprises have been well chosen, and its subscribers will find that it gives them every opportunity of keeping their knowledge up-to-date. The second part of the catalogue containing a classified index of subjects with the names of the authors who have treated them is a great convenience. For the benefit of book-buyers the published price of each book is stated, and subscribers to the library are given special facilities for obtaining second-hand copies of various works.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. cxlvii., No. 1, July 6, 1908.

Triboluminescence of Racemic Compounds.—D. Gernez.—The author has investigated the question of the possibility of the existence of a relation between the molecular constitution of certain substances and their triboluminescence, paying special attention to Tschugaeff's generalisation that when two constituents are triboluminescent the racemic compound formed by their union does not possess the same property. He has studied the tartrates more particularly, and the general conclusions he has drawn do not confirm Tschugaeff's view, and point to the fact that there is no connection between the triboluminescence of substances and their symmetrical or asymmetrical constitution.

Action of Metallic Oxides (Reducible) upon Primary Alcohols.—Paul Sabatier and A. Mailhe.—Certain reducible oxides, *e.g.*, Sb_2O_5, Sb_2O_3, Bi_2O_3, react with primary alcohols below 400°, giving water and aldehyde; neither gas nor acid is formed, and a semi-metallic mass is left. When the oxide is reduced more readily the aldehyde is partially oxidised, giving either the corresponding acid or water and carbon dioxide. Very often the metal or lower oxide which is formed catalytically decomposes the primary alcohol. Some of the oxides which are reduced by alcohol have a catalytic action on the latter, which lasts as long as any of the original oxide is left.

Relation between the Magnetic and Chemical Properties of Complex Salts containing Iron.—P. Pascal.—The determination of the magnetic susceptibility of different solutions of ferric chloride, $FeCl_3$, potassium ferricyanide, $Fe_2(CN)_{12}K_6$, sodium ferripyrophosphate, $Fe_2(P_2O_7)_3Na_6$, and ferrimetaphosphate, $Fe_2(PO_3)_{12}Na_6$, and ammoniacal ferric phosphate, shows that in this family of complex compounds of the same type the degradation of the chemical properties of iron, from the point of view of analysis, is accompanied by a parallel degradation of the magnetic properties. If the ferric complex is destroyed by an acid it is seen that the return towards the ferric state is accompanied by an increasing paramagnetism.

New Iodide of Titanium, TiI_2.—Ed. Defacqz and H. Copaux.—To prepare the new lower iodide of titanium two boats, one of which contains the tetraiodide and the other mercury, are heated side by side in a porcelain tube through which a current of dry hydrogen is passed. Thus a sublimate is formed which consists of crystals of the di-iodide. This substance is black and shining, infusible, not volatile, and very hygroscopic. It is not reduced by hydrogen at a dark red heat, but yields amorphous titanium at a white heat. The chloride is obtained when it is gently heated in a current of chlorine. Oxygen decomposes it into iodine and titanic acid. Sulphur and phosphorus react upon it at their melting-points, giving the corresponding compounds. Nitric and sulphuric acids attack it violently in the cold, setting free iodine. Gaseous ammonia gives an addition product.

Heat of Neutralisation of Picric Acid by different Aromatic Bases in Benzene.—Léo Vignon and M. Evieux.—From the heat of neutralisation of various picrates in benzene it may be deduced that the formation of salts may take place, but the formation differs from that which occurs in water. Since benzene possesses practically no ionising power it is specially valuable for use in the thermic study of the formation of certain salts. The presence of several NO_2 groups in the radical combined

with OH makes the acid function very strong. Picric acid does not behave like an acid towards certain bases such as *o*-nitraniline. Some other substances, for instance trichloracetic acid, in which the acid character is strengthened by the substitution of 3Cl for 3H, behave in the same way as picric acid.

Direct Transformation of Borneol into Campholic and Isocampholic Acids.—Marcel Guerbet.—When borneol is heated with freshly fused potash it is transformed nearly quantitatively into campholic and isocampholic acids as shown by the equation $C_{10}H_{18}O + KOH = C_{10}H_{17}KO_2 + H_2$. The acids in the alkaline solution may be separated by adding sulphuric acid till the liquid is feebly acid, then passing in carbon dioxide and cooling with ice-water. The campholic acid is thus precipitated. The isocampholic acid can be separated by adding sulphuric acid to the filtrate, and it may be purified by crystallising its calcium salt in absolute alcohol. This transformation of borneol into campholic acid is interesting, because it is probably the type of the action of potash at high temperatures upon secondary cyclanols.

Preparation of Benzoylacetic Ethers.—A. Wahl.—When ethyl benzoate and sodium are brought together in anhydrous ether three reactions occur simultaneously:—Sodium acts upon the acetic ether, giving ethylacetylacetate; sodium acts upon the benzoic ether, giving benzoïn; and finally sodium acts upon the mixture of the two ethers, giving ethyl benzoyl acetate. In order that this last may be the predominating reaction care must be taken that the benzoic ether is not in contact with an excess of sodium, and also that the metal is not present in an excess of acetic ether. The author has also shown that the condensation of methyl benzoate and acetate readily yields methyl benzoylacetate, from which the ethers of benzoylacetic acid with higher alcohols can easily be prepared.

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The MEDICAL SESSION will be opened on MONDAY, the 12th OCTOBER, 1908.

WINTER COURSES.

Zoology, Elementary, 9 a.m.; and Zoological Laboratory, Elementary, 11 a.m. or 3 p.m.—Professor Graham Kerr, M.A.
Chemistry, 10 a.m.; and Chemical Laboratory, 10 a.m. to 4 p.m.—Professor Ferguson, M.A., LL.D., F.S.A.
Organic Chemistry, Elementary.—T. S. Patterson, Ph.D.
Anatomy, Junior, 11 a.m.; Senior, 1 p.m.; and Practical Anatomy, 9 a.m. to 4.45 p.m.—Professor Cleland, M.D., LL.D., D.Sc., F.R.S., and Demonstrators.
Applied Anatomy (Jan.).—Robert Kennedy, M.A., D.Sc., M.D.
Physiology, 12 noon; Practical Physiology; and Physiological Laboratory.—Professor Noel Paton, B.Sc., M.D., and Assistants.
Physiological Chemistry.—E. P. Cathcart, M.D.
Psychological Physiology.—Henry J. Watt, M.A., Ph.D.
Materia Medica and Therapeutics, 11 a.m.; and Pharmaceutical Laboratory. Professor Stockman, M.D.
Pathology, Systematic, 3 p.m.—Professor Muir, M.A., M.D.
Surgery, 12 noon.—Prof. Sir William Macewen, M.D., LL.D., F.R.S.
Midwifery, 2 p.m.—Professor Murdoch Cameron, M.D.
Practice of Medicine, 11 a.m. Professor Gemmell, M.D.
Clinical Medicine, 9 a.m.—Professor Gemmell, M.D.
Clinical Surgery, 9.15 a.m.—Professor Sir Hector C. Cameron, M.D., and Professor Sir William Macewen, M.D., LL.D., F.R.S.
Public Health, 12 noon, four days weekly; Public Health Laboratory, 10 a.m. to 4 p.m.—Professor Glaister, M.D., D.P.H. (Camb.).
Ear, 4 p.m, Mon. (University); Practical Instruction as may be arranged.—Thomas Barr, M.D.
Throat and Nose, 4 p.m., Thurs. (University); Tues. or Fri. (Western Infirmary). James Walker Downie, M.B.

SUMMER COURSES.

Commencing on TUESDAY, 20th APRIL, 1909.

Physics, 11 a.m. James G. Gray, B.Sc.
Practical Physics, 9 to 11 a.m., or 1 to 3 p.m.—Professor Gray, M.A., LL.D., F.R.S.
Botany, 8 a.m.; and Botanical Laboratory, 9 a.m to 4 p.m.—Professor Bower, Sc.D., F.R.S.
Clinical Medicine, 9 a.m.—Professor Gemmell, M.D.
Clinical Surgery, 9.15 a.m.—Professor Sir Hector C. Cameron, M.D., and Professor Sir William Macewen, M.D., LL.D., F.R.S.
Chemical Laboratory, 10 a.m. to 4 p.m.—Professor Ferguson, M.A., LL.D., F.S.A.
Organic Chemistry, Elementary.—T. S. Patterson, Ph.D.
Practical Anatomy, 9 a.m. to 4 p.m.—Professor Cleland, M.D., LL.D., D.Sc., F.R.S., and Demonstrators.
Embryology, 11 a.m.; and Embryological Laboratory, 9 a.m. to 4 p.m. James F. Gemmell, M.A., M.D.
Applied Anatomy.—Robert Kennedy, M.A., D.Sc., M.D.
Practical Pharmacy, 12 noon.—Professor Stockman, M.D.
Practical Physiology, 8 to 10 or 9 to 11 a.m.; and Physiological Laboratory.—Professor Noel Paton, B.Sc., M.D., and Assistants.
Medical Jurisprudence and Public Health, 11 a.m.; and Public Health Laboratory.—Professor Glaister, M.D., D.P.H. (Camb.).
Practical Pathology, 1 to 3 p.m.—Professor Muir, M.A., M.D.
Operative Surgery, 12 noon, with practical work at other hours.—Professor Sir William Macewen, M.D., LL.D., F.R.S.
Diseases of Women, 2 p.m., Tu., Th., Fri.—Professor Murdoch Cameron, M.D.
Insanity, 12 noon, Wed. (University); 10 a.m., Sat. (Gartnavel).—Landel R. Oswald, M.B.
Ear, 4 p.m., Mon. (University); Practical Instruction as may be arranged.—Thomas Barr, M.D
Throat and Nose, 4 p.m., Thur. (University); Tues. or Fri. (Western Infirmary).—James Walker Downie, M.B.

Western Infirmary.—This Hospital, near the University, contains over 500 Beds for Medical and Surgical Patients, including Wards for Skin Diseases, and two for Diseases peculiar to Females.

Degrees.—Four Medical Degrees are conferred under the new Regulations, viz., Bachelor of Medicine (M.B.) and Bachelor of Surgery (Ch.B.), which must be taken together; Doctor of Medicine (M.D.), and Master of Surgery (Ch.M.); all of which are recognised by the Medical Acts as qualifying for Practice throughout the British dominions. The Degrees of B.Sc. and D.Sc. in Public Health, and of B.Sc. in Pharmacy, are also conferred.

Fees.—The Fee for each Systematic Class is, as a rule, £4 4s. The Fee for M.B. and Ch.B. is £23 2s.; for M.D., £10 10s.; for Ch.M., £10 10s.; for B.Sc., £6 6s.; for D.Sc., £10 10s.

Bursaries.—Bursaries to the annual amount of upwards of £1000 are restricted to Medical Students, whilst Scholarships and Fellowships to the amount of upwards of £1600 may be held by Medical Students who have gone through the Arts Course.

Full particulars as to the Course of Education and Examination required for the Degrees, and the Preliminary Examination required to be passed by Students before beginning Medical study, will be found in the University Calendar (by post 3s. 4d.); or a Syllabus of the Regulations, Fees, &c., may be obtained by applying to Mr. W. Innes Addison, Assistant Clerk of Senate.

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A NEW THEORY OF MOLECULAR VOLUMES.

By GERVAISE LE BAS, B.Sc.

Introduction.

It is more than fifty years (1855) since Kopp applied his additive theory of molecular volumes to organic compounds at the boiling-point. Starting from the fundamental observation that the volume of the homologous increment, $CH_2 = 22 = constant$ at this point, he was led to the conclusion that the molecular volumes of compounds under such conditions are equal to the sums of their atomic volumes.

Subsequent observers have found that the theory of molecular volumes cannot be so simply stated, for—(*a*) the volume of CH_2, and by inference the atomic volumes, are not quite constant (Gartenmeister and Schiff; *cf.* also Young, in British Association Address, Cambridge, 1904); (*b*) it is slso evident that the volumes of compounds possessing the same composition and nearly the same constitution, as, for instance, the isomeric dihalogen organic compounds (Städel), do not possess quite the same volumes at the boiling-point.

These and similar observations show that a simple additive theory does not hold good. It then becomes necessary to decide whether the above limitations require an abandoment of this view of molecular volumes, as has been done by Traube, or whether they are to be considered as due to constitutive influences.

That there is a great deal to be said in favour of an additive theory is evident from Kopp's own observations, as well as from the wealth of material that has since been accumulated, but especially by Thorpe's researches, which include determinations of molecular volumes of compounds which are usually regarded as inorganic (*Journ. Chem. Soc.*, 1880). Ostwald ("Lehrb. der Allg. Chem.," 2nd Edit., 1891, p. 356), who has made a thorough epitome of the material, has shown that simple additive relations exist, with some very considerable deviations, which are to be ascribed to the influence of constitution.

The present theory of molecular volumes is based upon a number of propositions which are shown to be supported by experimental evidence. The *first* is as follows:—

I. *The molecular volumes of chemical compounds under corresponding conditions are entirely functions of their chemical composition and constitution.*

This proposition may be inferred from Van der Waal's equation of condition. According to this, $V_k = 3b = 3V_0$; that is, the molcular critical volume is equal to three times the constant *b*, which represents the molecular volume at absolute zero. *b*, that is V_0 and therefore V_k, are measures of the space occupied by the molecules, and thus similar volume relations hold under all these conditions, and also more or less under conditions that are equally reduced, as, for example, at equal fractions of the critical pressures. The probability, however, is that V_0 is $\frac{1}{4}$ rather than $\frac{1}{3}$ of V_k, but this circumstance of course does not affect the volume relations.

The *second* principle is—

II. *That the molecular volumes under corresponding conditions are partly additive and partly constitutive.*

Kopp advocated an additive theory pure and simple, but observation shows that it is not true. Nevertheless, the additive principle is to a large extent valid. It will be necessary, in the first place, to correct Kopp's atomic volumes, especially those of the fundamental atoms C and H. This correction has the effect of allowing the question of influence of constitution to be more readily discussed, for then a relation is discoverable between differences in volume and the differences in constitution which are known to exist between the members of the different classes of compounds.

So far, the effect of constitution has not been very precisely defined nor studied with any degree of completeness.

Almost the only generalisation of importance coming under this head is—

That the volumes of compounds diminish more and more as the shape of the molecules tend towards the spherical.

It is, however, difficult to understand why such a relatively small difference in the constitution of such compounds as the normal and iso paraffin hydrocarbons, for example, should be measurable in terms of volume, while the very great constitutive differences which exist between the hydrocarbons hexane, benzene, naphthalene, and anthracene should not be noticeable in their molecular volumes. It is evident from the following that there are considerable differences between the volumes of compounds possessing the same composition which can only be ascribed to differences in constitution.

Thus a difference of 12·5 exists between the volumes of *heptylene* and *hexahydrotoluene*, both of which possess the empirical formula C_7H_{14}, and also a difference of 13·2 between the volumes of *cymene* and *hexahydronaphthalene* of formula $C_{10}H_{14}$. These differences are not accounted for on Kopp's hypothesis—although he was aware of their existence, and thus there appears to be in it a deficiency of capital importance.

The *constitutive influences* which might conceivably affect the molecular volumes of compounds are:—

a. Change of valency of one or more of the constituent atoms.
b. The complexity of the compounds.
c. The arrangement of the atoms in the molecule.

(No notice is here taken of association, as it does not appear to affect molecular volume very considerably, if at all).

A consideration of the influence of (*a*) on the molecular volume is reserved till later.

It appears that the complexity of a compound is a factor influencing the volume to a slight extent. This is shown by the fact that the volume of the homologous increment CH_2 varies slightly from compound to compound. Consequently, the atomic volumes may be supposed to differ. It nevertheless follows that the apparent volume of CH_2 is not usually the true one, for its magnitude depends on the changes which may occur from compound to compound, influencing every atom proportionately, and not only the increment CH_2.

Young has shown (British Association Address, Cambridge, 1904) that, under all conditions, the apparent volume of CH_2 is not constant. In Table I. it is found that the molecular volumes and the differences Δ are given under the following conditions:—

A. At 0° C.
B. At the respective boiling-points under 1 atmosphere pressure.
C. At equally reduced temperatures (0·6396).
D. At the respective boiling.points under equally reduced pressures (0·02241).
E. At the respective critical-points.

The variation of the differences under the above conditions is thus undoubted. This confirms the older work by Gartenmeister on the ethereal salts of the fatty acids. In order to show that the apparent volume of CH_2 is not the true one the following considerations are submitted:—It is shown (*loc. cit.*) that there exists the relation $C = 4H$ between the volumes of the atoms C and H, so that it is merely necessary to divide the molecular volumes of the normal paraffins by an arithmetical series—similar to that

TABLE I.—*Volume of* CH_2 *in the Normal Paraffins under various Conditions (Young).*

Paraffin.	A. Mol. vol.	A. Δ.	B. Mol. vol.	B. Δ.	C. Mol. vol.	C. Δ.	D. Mol. vol.	D. Δ.	E. Mol. vol.	E. Δ.
n-Butane ..	—		96	21·80	—		—		251·0	58·3
n-Pentane ..	111·33	15·44	117·8	22·13	116·13	20·09	116·13	20·66	309·3	56·8
n-Hexane ..	126·77	15·69	139·93	22·63	136·22	20·18	137·19	21·49	366·1	60·2
n-Heptane ..	142·46	15·88	162·56	23·70	156·40	20·54	158·68	21·83	426·3	62·6
n-Octane ..	158·34		186·26		176·94		180·51		488·9	

TABLE II.—*The Volumes of* CH_2, *apparent and real, at the Boiling-point and at equally Reduced Pressure.*

Hydrocarbon.	W.	Mol. vol. at boiling-point.	Δ.	6 V/W.	Mol. vol. for $P/P_k = 0{\cdot}01179$.	Δ.	6 V/W.
n-Butane, C_4H_{10} ..	26	96	21·80	22·15	—	11·11	—
n-Pentane, C_5H_{12} ..	32	117·8	22·13	22·08	116·13	21·06	21·77
n-Hexane, C_6H_{14} ..	38	139·93	22·63	22·09	137·19	21·49	21·66
n-Heptane, C_7H_{16} ..	44	162·56	23·70	22·17	158·68	21·83	21·64
n-Octane, C_8H_{18} ..	50	186·25		22·35	180·51		21·66

TABLE IV.—*Showing the Values of* V/W *at the Boiling- and the Critical-points.*

No.	Hydrocarbon.	W.	V (b. p.).	Δ.	V/W.	V *k*.	Δ.	V/W.
1.	*n*-Butane, C_4H_{10}	26	95·9	21·9	3·69	251·0	58·3	9·65
2.	*n*-Pentane, C_5H_{12}.. ..	32	117·8	22·13	3·68	309·3	56·8	9·67
3.	*n*-Hexane, C_6H_{14}	38	139·93	22·63	3·68	366·1	60·2	9·63
4.	*n*-Heptane, C_7H_{16} . ..	44	162·56	23·70	3·69	426·3	62·5	9·69
5.	*n*-Octane, C_8H_{18}	50	186·26		3·72	488·9		9·78
	Mean values				3·69			9·68

TABLE V.—*Volumes of the Normal Paraffin Hydrocarbons taken under Reduced Pressures.*

Reduced pressure.	Pentane, C_5H_{12}. W = 32. M.V.	V/W.	Hexane, C_6H_{14}. W = 38. M.V.	V/W.	Heptane, C_7H_{16}. W = 44. M.V.	V/W.	Octane, C_8H_{18}. W = 50. M.V.	V/W.
1·000000	309·20	9·66	366·30	9·64	425·7	9·67	488·9	9·77
0·82568	193·80	6·05	229·20	6·03	265·25	6·03	305·2	6·10
0·44232	153·85	4·808	181·80	4·784	210·36	4·781	241·11	4·822
0·144744	131·25	4·101	155·09	4·082	179·62	4·082	204·62	4·092
0·04232	120·15	3·755	141·95	3·736	164·02	3·728	187·02	3·740
0·022411	116·13	3·629	137·19	3·610	158·68	3·606	180·51	3·610
0·011795	113·20	3·537	133·65	3·517	154·58	3·513	175·83	3·517

of the valency numbers—to obtain the true volumes of H in each compound, and so the volumes of CH_2.

The assumption is, of course, made that all the atoms C and H obey the 4 : 1 rule in every individual compound. This is justified, for $H_2 = C_nH_{2n+2} - nCH_2 = \frac{1}{3}CH_2$, as will be seen. A comparison of the substances is made.

a. At the boiling-point under 1 atmosphere pressure.

b. Under identically reduced pressures $P/P_k = 0{\cdot}01179$.

Since V/W represents the volume of H, W standing for the valency number of the compound, 6V/W represents the true volume of CH_2 in every individual compound.

Columns 4 and 7 give the true volumes of CH_2 under the above conditions, and it is seen that the molecular volumes are much more nearly additive than is shown by the apparent volumes of CH_2.

It must be remarked, however, that the changes from compound to compound are greater for more complex compounds than the above. A further consideration of this matter is reserved.

The above evidence, and also some to be afterwards mentioned, makes it clear that the limitations of the additive theory indicated by the variation of CH_2 is explained in the following way :—

III. *Although the volumes of like atoms are usually the same in a single compound they are yet susceptible to slight changes from compound to compound, but in such a way as to preserve the characteristic relationship between the volumes of dissimilar atoms.*

The above principle not only indicates the fact of variation of the molecular volume with the complexity of the compound, but also the manner of such variation.

A *fourth* principle shows the effect of a particular method of arrangement, namely, that of ring structure. It is as follows :—

IV. *The atomic volumes are smaller in a closed than in an open chain compound. The total diminutions which are characteristic of certain classes of compounds are functions not only of the number of atoms in a ring, but also of the number of rings.*

The method of finding these total diminutions is to deduct the molecular volume of the ring compound from the sum of the atomic volumes found from a consideration of open chain series. Another way of stating this is that the diminutions represent the differences between the volumes of the ring compounds and the volumes of similar complexes in the open chain series. From the fact that the diminutions are similar for the same class of compounds, it is concluded that the relative volumes of the atoms in ring compounds are similar to the relation between their volumes in the open chain series—a fact which further proves the validity of Principle III.

The following figures illustrate the importance of Generalisation IV., which shows the effect of ring structure on molecular volumes.

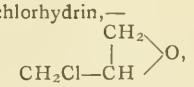
It will be necessary to account for smaller volume differences by slighter differences in arrangement, but this can only be done by a careful study of accurate data. As it has already been stated, one generalisation of importance has been given.

TABLE III.

	Contraction.
Three-membered single ring—	
Epichlorhydrin, C_3H_5ClO	−5·2
Four-membered single ring—	
Diamylene, $C_{10}H_{20}$	−10·7
Five-membered ring—	
Thiophene, C_4H_4S	−11·5
Six-membered single ring—	
Paraldehyde, $C_6H_{12}O_3$	−15·8
Benzene, C_6H_6	−15·0
Carvene, $C_{10}H_{16}$	−16·9
Double ring—	
Pinene, $C_{10}H_{16}$	−25·7
Naphthalene, $C_{10}H_8$	−30·4
Camphor, $C_{10}H_{16}O$..	−30·6
Triple ring—	
Anthracene, $C_{14}H_{10}$	−48·7

A point of very great practical importance is that ring compounds, which are immediately derived from members of the open chain class of compounds like diamylene and paraldehyde—which are formed by the polymerisation of amylene and aldehyde respectively—are equally subject to contractions with such typical ring compounds as benzene and pyridine.

The case of epichlorhydrin,—



which is a very simple ring compound, shows the large diminution of −5·2; that is, its volume is smaller by 5·2 units than that of its theoretical isomer, $CHCl=CH—CH_2OH$. These facts show that we have here a valuable aid in the elucidation of chemical structure

It is thus clear that molecular volumes take into account two great types of structure, the open and closed chain, which types the theory of linking of atoms foreshadows, and which are completely identified by modern methods of chemical investigation.

It must be particularly observed that the above principles are not of the nature of explanations, so much as facts which require explanation. The nature of the latter must depend on the precise meaning to be attached to the term "atomic volume." This involves the far-reaching question of liquid structure about which very little is known.

The Atomic Volumes of C *and* H.—Kopp concluded from his observations that C = 11 and H = 5·5, so that C = 2H. Schröder's relation was C = H.

Neither of these relations are admissible (see *Phil. Mag.*, [6], No. 81, xiv., p. 338); Kopp's numbers were obtained by a comparison of the volumes of such differently constituted bodies as butane C_4H_{10}, and benzene C_6H_6, for example; and thus it was concluded that the very great differences in the constitutions of these compounds produce no effect on their molecular volumes. Since, however, molecular volumes are only in part additive, this would *à priori* appear improbable. It is far better to obtain the atomic volumes of C and H by comparing the volumes of related compounds, such as those belonging to the fatty series.

I. *The Volumes* C *and* H *in the Normal Saturated Paraffins.*

A point which is worthy of notice is that the molecular volumes of the normal paraffin hydrocarbons are proportional to their valency numbers at the boiling- and the critical-points, and indeed under all corresponding conditions, especially at identically reduced pressures (see *Phil. Mag.*, Sept., 1907, [6], No. 81, xiv., pp. 337—344). If V represents the molecular volume and W the valency number, then V/W is approximately constant under the above conditions.

The constancy of V/W is in each case far greater than the differences for CH_2 would lead us to expect, especially at the critical temperature. Since the latter are necessarily subject to perturbations which more or less mask the true value of CH_2, it is better to obtain it from the value of V/W, which represents the volume of H. Thus, $6\times3·69 = 22·1$ (approx.).

Now,—

$$C_nH_{2n+2} = nCH_2 + H_2,$$

and therefore,—

$$\begin{aligned} H_2 &= C_nH_{2n+2} - nCH_2 \\ H_2 &= (C_4H_{10}) - 4(CH_2) = 95·9 - 88·4 = 7·5 \\ &= (C_5H_{12}) - 5(CH_2) = 117·8 - 110·5 = 7·3 \\ &= (C_6H_{14}) - 6(CH_2) = 139·93 - 132·6 = 7·33 \end{aligned}$$

Mean value of H_2 = 7·38

The direct determination of the volume of H at the boiling-point is—

$$H = \frac{7·38}{2} = 3·69,$$

and since $CH_2 = 22·1$, therefore $C = 22·1 - 7·38 = 14·72 = 4\times3·68$.

The relation C = 4H is thus the true one. At the critical-point the true value of CH_2 is $6\times9·68 = 58$, so that—

$$\begin{aligned} H_2 &= 251 - 23·2 = 19 \quad \text{for } C_4H_{10} \\ &= 309·3 - 290 = 19·3 \text{ for } C_5H_{12} \\ &= 366·1 - 348 = 18·1 \text{ for } C_6H_{14} \\ &= 426·3 - 406 = 20·3 \text{ for } C_7H_{16} \end{aligned}$$

Mean value of H_2 = 19·2 (approx).

The volume of H at the critical-point is thus approx.,—

$$\frac{19·2}{2} = 9·6,$$

and since $CH_2 = 58$, $C = 58 - 19·2 = 38·8 = 4\times9·7$.

The relation C = 4H is also true at the critical-point.

The difference for CH_2 is about the same in all the fatty series. It is thus concluded that carbon and hydrogen occupy similar volumes in the saturated hydrocarbon residues that they do in the normal paraffin hydrocarbon series.

It has been shown that the relation C = 4H holds at the melting-point and at equal intervals of temperature therefrom in the complex hydrocarbons from undecane $C_{11}H_{23}$, to pentatriacontane $C_{35}H_{72}$. Here, however, V/W, that is to say, H = 2·970 exactly, and $C = 4\times2·970 = 11·88$ (*Phil. Mag.*, Sept., 1907, No. 81, pp. 324—334).

The relation C = 4H is also true under conditions of equally reduced pressures, in the case of the simple normal paraffins, from pentane to octane (Table V.). (For data see Young, *Journ. Chem. Soc.*, 1895—1900).

The Unsaturated Hydrocarbons.—It is remarkable that the volumes of the olefines and the acetylenes are also proportional to their valency numbers, from which it follows that the relation C = 4H holds. The atomic volumes of C and H are C = 14·8 and H = 3·7. This furnishes a means of verifying the above numbers in a direct way (see Table VI.).

TABLE VI.—*The Volumes of the Atoms* C *and* H *in Unsaturated Compounds at the Boiling-point.*

Compounds.	W.	V.	Δ for $n(H_2)$.	V/W.	Authority.
Pentane, C_5H_{12} ..	32	117·8	$2\times3·95$	3·68	Young
Amylene, C_5H_{10}..	30	109·9	$4\times3·32$	3·67	Schiff
Valerylene, C_5H_8.	28	104·5		3·73	Buff
Hexane, C_6H_{14}..	38	139·93	$2\times3·70$	3·68	Young
Hexylene, C_6H_{12} .	36	132·4	$4\times3·53$	3·68	Schiff
Diallyl, C_6H_{10} ..	34	125·8		3·71	Schiff
Heptane, C_7H_{16}..	44	162·56	$2\times3·88$	3·69	Young
Heptylene, C_7H_{14}	42	154·58		3·68	Schiff
Octylene, C_8H_{16} .	48	177·6		3·70	Young
Mean values ..			$14\times3·58$	3·69	

The value of V/W is found to be approximately constant in the unsaturated compounds, and the approximate value of H is shown by the differences, although the latter are necessarily somewhat irregular, being small numbers.

It nevertheless follows that V/W = H.

If the unsaturated members of other fatty series are also considered, the same differences for H_2 appear, so that additive relations are also found to be true for such compounds (Table VII.).

TABLE VII.—*The Volume of* H *in the various Fatty Series.*

P compounds.	V.	Δ.	Authority.
Propyl alcohol, C_3H_8O ..	81·3	2×3·55	Schiff
Allyl alcohol, C_3H_6O . ..	74·2		,,
Propyl amine, C_3H_9N ..	85·6	2×3·60	,,
Allyl amine, C_3H_5N.. ..	78·4		,,
Tripropyl amine, $N(C_3H_7)_3$	222·1	6×3·63	,,
Triallyl amine, $N(C_3H_5)_3$.	200·3		,,
Propyl acetate, $C_5H_{10}O_2$..	128·5	2×3·60	,,
Allyl acetate, $C_5H_8O_2$ ..	121·6		,,
Propyl chloride, C_3H_7Cl..	91·4	2×3·60	,,
Allyl chloride, C_3H_5Cl ..	84·2		,,
Mean value of H_2 ..		14×3·60	

The volume of H is shown by Table VII. to be the same in various fatty series as in the open chain hydrocarbons, saturated and unsaturated.

A similar direct method to the above of calculating the value of C is available (see Table VIII.).

TABLE VIII.—*The Volume of* C *in the "Straight Chain" Hydrocarbons.*

Hydrocarbon.	V.	Δ for C.
Butane, C_4H_{10}	95·9	14·0
Amylene, C_5H_{10}.. ..	109·9	16·0
Diallyl, C_6H_{10}	126·1	
Pentane, C_5H_{12}	117·8	14·6
Hexylene, C_6H_{12} . ..	132·4	
Hexane, C_6H_{14}	139·93	14·87
Hexylene, C_7H_{14} . ..	154·8	
Heptane, C_7H_{16}.. ..	162·56	15·04
Octylene, C_8H_{16}.. ..	177·6	
Mean value of C ..		14·9

Since the above numbers for C and H approximately agree with those found by considering the normal paraffins at the boiling point, it does not appear that unsaturation has any special effect on the molecular volumes under the above conditions.

The conclusion is that at the boiling-point the volumes of carbon and hydrogen in the aliphatic class of compounds are C = 14·8, H = 3·7, *subject to augmentations as complexity increases, and that under corresponding conditions there exists the relation* C = 4H *between the atomic volumes* C *and* H.

The molecular volumes of the hydrocarbons at the boiling-point can thus be calculated by means of the following equations:—

Mol. vol of—

Normal paraffins $C_nH_{2n+2} = (6n+2)S = WS$
Olefines .. .. $C_nH_{2n} = (6n S) = WS$ $S = 3·70$
Acetylenes .. $C_nH_{2n-2} = (6n-2)S = WS$

(W represents the valency numbers).

The above atomic values of C and H are quite different from those of Kopp, C = 11 and H = 5·5. This change in the fundamental atomic values entails very important consequences in the molecular volume theory.

(To be continued).

THE

RELATION BETWEEN THE CRYSTALLINE FORM AND THE CHEMICAL CONSTITUTION OF THE PICRYL DERIVATIVES.*

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THE general relation existing between the constitution and the crystalline form of chemical substances has been determined by Barlow and Pope (*Trans. Chem. Soc.*, 1906, lxxxix., 1675; 1907, xci., 1150). It is conveniently illustrated by assigning to each atom present a sphere or domain of influence, and constructing homogeneous close-packed assemblages corresponding in composition and constitution to the compounds concerned, using spheres as structural units to represent the spheres of atomic influence. On constructing such assemblages it is found that, for their dimensions to accord with the geometrical dimensions of the crystal, the spheres of influence, delimited by the polyhedral cells enclosed by tangent planes drawn through the points of contact of neighbouring spheres, must possess volumes approximately proportional to the fundamental valencies of the corresponding elements. The assemblages derived in this way exhibit properties corresponding with the chemical composition and constitution, and with the crystalline form of the substance represented; they are found also to be homogeneously partitionable into units which correspond in configuration with the chemical properties of the substance.

The method of treatment here briefly indicated has been applied and tested to such an extent as proves its general applicability, and demonstrates that the principle involved is the correct one (Jaeger, *Trans. Chem. Soc.*, 1908, xciii., 517); the conclusion that the fractions of the molecular volume appropriated by the component atoms are approximately proportional to the valencies of the respective elements has also been substantiated by independent work on the subject of molecular volumes (Le Bas, *Trans. Chem. Soc.*, 1907, xci., 112; *Phil. Mag.*, 1907, xiv., 324).

As the theory indicates that the crystalline forms exhibited by related substances are derivable in a comparatively simple manner one from the other, it is desirable that groups of allied organic substances should be examined, as far as possible, by aid of the new method, We have therefore studied the whole of the crystallographic data available for the derivatives of the symmetrical radicle, picryl, namely, 1 : 3 : 5-trinitrophenyl, $C_6H_2(NO_2)_3$, and for purposes of comparison have determined experimentally the geometrical constants of several related substances.

Two distinct assemblages can be devised, both in accordance with the crystallographic and chemical data, to represent the crystal structure of benzene and its simple derivatives (*Trans. Chem. Soc.*, 1906, lxxxix., 1692); it has been shown that both these forms of assemblage can be traced among the simple derivatives of benzene. The first assemblage is derivable from the closest-packed assemblage of equal spheres of hexagonal type (*loc. cit.*, p. 1699), and, taking the volume of a monovalent sphere of atomic influence as unity, the dimensions of a unit of the partitioning of the assemblage, namely, of the benzene molecule itself, are determined by the following rectangular co-ordinates:—

$$x : y : z = 3·101 : 3·480 : 2·780.$$

These values constitute the so-called equivalence parameters for benzene and their product; the valency volume, W = 30, is the sum of the valencies of the atoms composing the benzene molecule, C_6H_6.

The second form of assemblage met with among the simple derivatives of benzene is derived from the closest-packed assemblage of equal spheres of cubic type, and is therefore of rhombohedral marshalling; it differs dimen-

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Table I.—*Crystal System (Orthorhombic).*

$a : b : c = 1{\cdot}8914 : 1 : 1{\cdot}3871.$

Forms observed: $a\{100\}$, $c\{001\}$, $r\{201\}$, $q\{021\}$, and $o\{111\}$.

Angle.	Number of observations.	Limits.	Mean.	Calculated.
001 : 201	15	55° 33′ to 55° 56′	55° 42′ 50″	—
100 : 111	12	66 34 „ 66 53	66 47 10	—
001 : 111	20	57 21 „ 57 58	57 32 20	57° 29′ 30″
111 : 1$\bar{1}$1	8	64 49 „ 65 17	64 59 0	65 1 0
201 : 20$\bar{1}$	5	68 21 „ 68 58	68 35 40	68 34 10
201 : 111	9	50 56 „ 51 20	51 5 30	51 3 50
111 : 021	4	27 45 „ 27 51	27 47 0	27 55 10
001 : 021	2	70 17 „ 70 22	70 19 30	70 10 40

Table II.—*Crystalline System (Hexagonal).*

$a : c = 1 : 1{\cdot}3890.$

Forms observed: $\{10\bar{1}1\}$, $\{10\bar{1}0\}$, $\{11\bar{2}0\}$, and $\{0001\}$.

Angle.	Number of observations.	Limits.	Mean.	Calculated.
$\bar{1}011 : 01\bar{1}1$	8	50° 17′ to 50° 3′	50° 12′ 40″	—
$000\bar{1} : 01\bar{1}1$	15	57 45 „ 58 25	58 2 50	58° 3′ 20″
$\bar{1}120 : 01\bar{1}1$	6	42 37 „ 43 5	42 43 30	42 42 10
$\bar{1}010 : \bar{1}011$	5	31 42 „ 32 5	31 57 0	31 56 40

Table III.

Substance.	$x : y : z$	β.	W.	Crystal system.
Substances of hexagonal marshalling—				
C_6H_6 ($y : z : x$)	3·480 : 2·780 : 3·101	90°	30	Orthorhombic.
1 : 3 : 5-$C_6H_2(NO_2)_3ONH_4$ . ..	5·251 : 2·776 : 3·852	90°	56	„
1 : 3 : 5-$C_6H_2(NO_2)_3OK$	5·082 : 2·699 : 3·647	90°	50	„
1 : 3 : 5-$C_6H_2(NO_2)_3CO_2H$.. ..	4·816 : 2·753 : 4·334	90°	56	„
1 : 3 : 5-$C_6H_2(NO_2)_3OCH_3$.. ..	4·843 : 2·811 : 4·115	89° 1′	56	Monosymmetric.
1 : 3 : 5-$C_6H_2(NO_2)_3NH_2$	4·815 : 2·873 : 3·814	80° 11′	52	„
1 : 3 : 5-$C_6H_2(NO_2)_3CH_3$	5·206 : 2·777 : 3·735	90°	54	Orthorhombic.
1 : 3 : 5-$C_6H_2(NO_2)_3Cl$	5·013 : 2·804 : 3·414	89° 56′	48	Monosymmetric.
1 : 3 : 5-$C_6H(NO_2)_3(OH)_2$	4·825 : 2·786 : 3·869	90°	52	Hexagonal.
1 : 3 : 5-$(NO_2)_3C_6(OH)_3,H_2O$ ..	4·822 : 2·784 : 4·320	90°	58	„
Substances of rhombohedral marshalling—				
1 : 3 : 5-$C_6H_3(NO_2)_3$	4·921 : 2·579 : 3·781	90°	48	Orthorhombic.
1 : 3 : 5-$C_6Br_3(NO_2)_2CH_3$	4·909 : 2·561 : 3·831	$\alpha = 85°$ 12′	48	Monosymmetric.
1 : 3 : 5-$C_6H_2(NO_2)_3OH$	3·706 : 3·596 : 3·572	90°	50	Orthorhombic.
1 : 3 : 5-$C_6H_2(NO_2)_3I$	3·660 : 3·583 : 3·660	90°	48	Tetragonal.

sionally from the hexagonal type by exhibiting a smaller z value and a larger y value than the former.

From the papers referred to it appears that among the simple derivatives of benzene the dimension z varies less than do the other two, namely, x and y; it would therefore seem that the adjustment of the assemblage which restores close-packing after the introduction of a substituting group into the benzene structure in general exerts itself mainly in the directions of x and y, and only affects but slightly the dimension z. The direction of z is that of the vertical dimension in the benzene molecule; that is to say, of the dimension perpendicular to the two planes containing the centres of the two sets of hydrogen atoms ordinarily numbered 1 : 3 : 5 and 2 : 4 : 6, respectively. It will be shown below that this approximate constancy of the vertical or z dimension is maintained in the more complex picryl derivatives.

Ammonium Picrate, C_6H_2—1 : 3 : 5—$(NO_2)_3$—ONH_4.

Ammonium picrate crystallises from water in orthorhombic forms; these have been measured by Handl (*Ber. k. Akad. Wien*, 1858, xxxii., 259) and by Laurent (*Revue Scient.*, ix., 26), who respectively assign to the substance the axial ratios:—

$$a : b : c = 1 : 0{\cdot}6787 : 0{\cdot}3569$$

and—

$$a : b : c = 1 : 0{\cdot}6873 : 0{\cdot}3652,$$

the mean values being—

$$a : b : c = 1 : 0{\cdot}6830 : 0{\cdot}3611.$$

Crystals much more suitable for exact measurement than these are obtained by crystallising the salt from acetone, in which it is fairly soluble; on allowing the acetone solution to evaporate spontaneously at the ordinary temperature, large transparent yellow crystals of hexagonal habit are deposited. The bright yellow colour of the crystals thus produced is quite distinct from the red tint sometimes assumed by ammonium picrate (Silberrad, *Trans. Chem. Soc.*, 1908, xciii., 477). The forms $a\{100\}$ and $c\{001\}$ are generally the best developed, and $q\{021\}$ was only observed on one crystal; the results obtained on measurement are given in Table I.

The form $o\{111\}$ has not previously been observed on

ammonium picrate crystals. The crystals exhibit a perfect cleavage on *a* {100}; this is also the optic axial plane, and the axis *b* is the acute bisectrix. The optic axial dispersion is very marked; the angle for red is much larger than that for yellow light.

The crystals deposited from water and from acetone are evidently of identical structure, for, on writing the axial ratios now given, namely,—

$$a : b : c = 1{\cdot}8914 : 1 : 1{\cdot}3871,$$

in the form—

$$a' : b' : c' = 1 : a/2c : 1/2c = 1 : 0{\cdot}6818 : 0{\cdot}3609,$$

he result is practically identical with the mean of the measurements of Handl and Laurent, namely,—

$$a : b : c = 1 : 0{\cdot}6830 : 0{\cdot}3611.$$

On calculating the equivalence parameters of ammonium picrate from our determination of the axial ratios, taking the valency volume of the molecule, $C_6H_2(NO_2)_3ONH_4$, as W = 56, the following values are obtained :—

$$x : y : z = 5{\cdot}251 : 2{\cdot}776 : 3{\cdot}582.$$

For comparison with these equivalence parameters it is convenient to calculate those of potassium picrate; this salt is orthorhombic with—

$$a : b : c = 1{\cdot}4352 : 1 : 1{\cdot}0616$$

(Brugnatelli, *Zeit. Kryst. Min.*, 1895, xxiv., 277), and by transposition the axial ratios may be obtained in the form—

$$a : b : c = 2 : 1{\cdot}0616 : 1{\cdot}4352 = 1{\cdot}8839 : 1 : 1{\cdot}3519.$$

The latter values show clearly the isomorphism of this salt with the previous one; the equivalence parameters of potassium picrate, $C_6H_2(NO_2)_3OK$, with W = 50 are calculated from the last form of the axial ratios as—

$$x : y : z = 5{\cdot}082 : 2{\cdot}699 : 3{\cdot}647.$$

It is seen that on passing from the potassium to the ammonium salt the principal increase amongst the equivalence parameters occurs in the directions *x* and *z*, whilst the value of *y* changes to a smaller extent, namely, from 2·699 to 2·776. The dimension *y* in the cases of these salts obviously corresponds to the dimension *z* = 2·780 in benzene itself. and this dimension, as remarked above, is the one of the three which tends to change least on simple substitution.

Ammonium picrate has the same valency volume, W = 56, as the orthorhombic 1 : 3 : 5-trinitrobenzoic acid, $C_6H_2(NO_2)_3CO.OH$, with the axial ratios—

$$a : b : c = 0{\cdot}8770 : 1 : 0{\cdot}5715$$

(Friedländer, *Zeit. Kryst. Min.*, 1877, i., 623), on interchanging in these axial ratios, *c* and *b*, *b* and *a*, and *a* and *c*, these values become—

$$a : b : c = 1 : 0{\cdot}5715 : 0{\cdot}8770 = 1{\cdot}7497 : 1 : 1{\cdot}5346.$$

This set of axial ratios corresponds to the equivalence parameters—

$$x : y : z = 4{\cdot}816 : 2{\cdot}753 : 4{\cdot}224.$$

The *y* value again corresponds closely to that of ammonium picrate and to the *z* value of benzene, so that on replacing the group, ONH_4, in the salt by the group, CO_2H of the same valency volume, W = 9, the vertical benzene dimension is sensibly preserved.

The methyl ether of picric acid 1 : 3 : 5 - trinitroanisol, $C_6H_2(NO_2)_3OCH_3$, also has the same constitution and valency volume, W = 56, as ammonium picrate; it crystallises in the monosymmetric system (Friedländer, *Zeit. Kryst. Min.*, 1879, iii., 173; compare Jaeger, *Ibid.*, 1905, xl., 565) with the axial ratios—

$$a : b : c = 1{\cdot}4635 : 1 : 2{\cdot}2211, \beta = 50^\circ 48'.$$

These axial ratios may be transposed by assigning to the planes (100), (10$\bar{1}$), and (110) the indices (10$\bar{1}$), (001), and (11$\bar{1}$), respectively, and then become—

$$a : b : c = 1{\cdot}7225 : 1 : 1{\cdot}4635, \beta = 91^\circ 51'.$$

The equivalence parameters corresponding to these axia ratios are—

$$x : y : z = 4{\cdot}843 : 2{\cdot}811 : 4{\cdot}115, \beta = 91^\circ 59' \text{ or } 89^\circ 1'.$$

The *y* value is again approximately equal to the *z* value for benzene and the substitution of the methoxyl group, $.OCH_3$, for $.ONH_4$ or $.CO_2H$, has effected but little change in the dimensions of the crystal structure.

Picramide, $C_6H_2(NO_2)_3NH_2$, which may be regarded as derived from ammonium picrate by the elimination of one molecule of water, crystallises in the monosymmetric system with (Friedländer, *loc. cit.*)—

$$a : b : c = 0{\cdot}838 : 1 : 0{\cdot}6638, \beta = 80^\circ 11'.$$

After dividing the length *b* by two, so that the axial ratios become—

$$a : b . c \quad 1{\cdot}676 : 1 : 1{\cdot}3276, \beta = 80^\circ 11',$$

and calculating the equivalence parameters, taking the valency volume as W = 52, the following values are obtained :—

$$x : y : z = 4{\cdot}815 : 2{\cdot}873 : 3{\cdot}814, \beta = 80^\circ 11'.$$

The *y* value differs rather more than before from the *z* value for benzene, but the *z* value is almost the same as for ammonium picrate.

The symmetrical trinitrotoluene,—

$$C_6H_2\text{-}1 : 3 : 5\text{-}(NO_2)_3\text{-}6\text{-}CH_3,$$

has a valency volume two units less than that of ammonium picrate and trinitroanisol, namely, W = 54, and crystallises in the orthorhombic system with—

$$a : b : c = 0{\cdot}9373 : 1 : 0{\cdot}6724$$

(Friedländer, *loc. cit.*). On dividing the length *b* by two, as in the previous case, so as to obtain the axial ratios in the form—

$$a : b : c = 1{\cdot}8746 : 1 : 1{\cdot}3448,$$

and calculating the equivalence parameters, the following values are obtained :—

$$x : y : z = 5{\cdot}206 : 2{\cdot}777 : 3{\cdot}735.$$

In this case both the *x* and *y* values are nearly identical with those for ammonium picrate, and the effect of the change of valency volume is thrown, in the main, upon the direction *z*.

Picryl chloride, $C_6H_2Cl\text{-}1 : 3 : 5\text{-}(NO_2)_3$, derived from picric acid by substituting chlorine for hydroxyl, has the valency volume, W = 48, and crystallises in the monosymmetric system with—

$$a : b : c = 1{\cdot}83288 : 1 : 0{\cdot}81135, \beta = 77^\circ 9'$$

(Bodewig, *Zeit. Kryst. Min.*, 1879, iii., 398). On transposing these axial ratios so that the planes (001), (10$\bar{1}$), (101), and (110) become respectively (103), (10$\bar{1}$), (301), and (110), the following values result :—

$$a : b : c = 1{\cdot}7875 : 1 : 1{\cdot}2175, \beta = 90^\circ 4'.$$

The corresponding equivalence parameters are—

$$x : y : z = 5{\cdot}013 : 2{\cdot}804 : 3{\cdot}414, \beta = 90^\circ 4' \text{ or } 89^\circ 56'.$$

The *y* dimension in this case also retains approximately its previous value.

Styphnic acid, $C_6H(OH)_2\text{-}1 : 3 : 5\text{-}(NO_2)_3$, the monohydroxy-derivative of picric acid, separates on spontaneous evaporation of its alcoholic solution in large straw-yellow prisms belonging to the hexagonal system; the results obtained on measurement are given in Table II.

The first angle quoted, namely, 50° 12′ 40″, has been given by Ditscheiner as 50° 12′ (*Annalen*, 1871, clviii., 247). On examining a section cut perpendicular to the principal axis, the uniaxial interference figure of the normal type is seen; the double refraction is strong and negative in sign. No indications were obtained of the hemimorphous development described by Lehmann (*Zeit. Kryst. Min.*, 1882, vi., 51).

For the purpose of comparing this substance with those

discussed above, its crystal form is conveniently referred to an orthorhombic axial system, in which the new ratio,—

$$a' : b' : c' = a\sqrt{3} : a : c = 1{\cdot}7321 : 1 : 1{\cdot}3890.$$

The equivalence parameters of styphnic acid, for which W = 52, are thence calculated as—

$$x : y : z = 4{\cdot}825 : 2{\cdot}786 : 3{\cdot}869.$$

The y value is again practically identical with the z value for benzene.

The symmetrical trinitrophloroglucinol crystallises with water, the crystals having the composition $C_6(OH)_3$-1 : 3 : 5-$(NO_2)_3,H_2O$, and belonging to the hexagonal system with—

$$a : c = 1 : 1{\cdot}0346$$

(Ditscheiner, *Zeit. Kryst. Min.*, 1881, v., 646). On increasing the length c by one-half and referring the axial ratios to an orthorhombic system of axes just as in the previous case, the axial ratios—

$$a : b : c = 1{\cdot}7231 : 1 : 1{\cdot}5519$$

are obtained. The equivalence parameters calculated from these values, taking W = 58, are—

$$x : y : z = 4{\cdot}822 : 2{\cdot}784 : 4{\cdot}320.$$

The values for x and y are practically identical with those for styphnic acid, so that the morphotropic effect of introducing the group, OH,H_2O, in place of a hydrogen atom in the styphnic acid assemblage is merely to increase the dimension z. Cases of very similar character to this occur among the minerals of the humite series and between camphoric anhydride and the addition compound of camphoric acid with acetone (*Trans. Chem. Soc.*, 1906, lxxxix., 1685).

The above results show that, by applying the method given by Barlow and Pope to the crystallographic data, an extensive series of picryl derivatives can be at once referred in a very simple manner to the hexagonal assemblage described for benzene. The following picryl derivatives seem to be derived from the alternative benzene assemblage, that, namely, which possesses the rhombohedral type of marshalling.

The symmetrical trinitrobenzene, 1 : 3 : 5-$C_6H_3(NO_2)_3$, is orthorhombic with the axial ratios (Friedländer, *loc. cit.*, p. 170)—

$$a : b : c = 0{\cdot}9540 : 1 : 0{\cdot}7330.$$

On dividing the length b by two, so as to obtain the axial ratios—

$$a : b : c = 1{\cdot}9080 : 1 : 1{\cdot}4660,$$

and calculating the equivalence parameters, with W = 48, the following values result :—

$$x : y : z = 4{\cdot}921 : 2{\cdot}579 : 3{\cdot}781.$$

The y value is in this case much smaller than among the previously discussed substances.

The 1 : 3 : 5-trinitrobenzene is identical in constitution and valency volume with the tribromo-1 : 3-dinitro-5-methylbenzene, and the two substances are morphotropically very closely related ; the latter is monosymmetric with—

$$a : b : c = 0{\cdot}5217 : 1 : 0{\cdot}7803,\ \beta = 85^\circ\ 12'.$$

(Jaeger, *Zeit. Kryst. Min.*, 1905, xl., 360). On interchanging the axial directions a and b, the axial ratios are obtained in the form—

$$a : b : c = 1{\cdot}9168 : 1 : 1{\cdot}4957,\ \alpha = 85^\circ\ 12'.$$

These values correspond to the equivalence parameters—

$$x : y : z = 4{\cdot}909 : 2{\cdot}561 : 3{\cdot}831,\ \alpha = 85^\circ\ 12'.$$

The above numbers show that in the passage from the symmetrical trinitrobenzene to the dinitrotribromotoluene of similar constitution, which results from replacing one nitro-group in the former by a methyl-group of the same valency volume, and replacing three hydrogen atoms by three bromine atoms, also of the same valency, practically no change is effected in the relative dimensions; the equivalence parameters are scarcely affected by the substitution.

It has been already remarked that the differences in dimensions between the benzene assemblages of hexagonal and of rhombohedral marshalling are greatest in the directions of y and z, so that the dimension x remains nearly the same in both. A similar correspondence would be expected to hold among the derivatives of benzene, and accordingly it is found that the x values, 4·909 and 4·921, of the dinitrotribromotoluene and the trinitrobenzene respectively, are nearly identical with the x value, 5·013, of picryl chloride, the three substances having the same valency volume.

These correspondences strongly indicate that the above two substances exhibit in their crystalline structure the second form of the benzene assemblage ; the same conclusion presumably holds for picric acid and picryl iodide, both of which crystallise in pseudo-cubic forms.

Picric acid crystallises in the orthorhombic system with—

$$a : b : c = 1{\cdot}0305 : 1 : 1{\cdot}0434$$

(Brugnatelli, *Zeit. Kryst. Min.*, 1895, xxiv., 277), and has the valency volume W = 50. The equivalence parameters are—

$$x : y : z = 3{\cdot}706 : 3{\cdot}596 : 3{\cdot}752.$$

Picryl iodide, C_6H_2I-1 : 3 : 5-$(NO_2)_3$, with W = 48, crystallises in the tetragonal system with—

$$a : c = 1 : 1{\cdot}958$$

(Fels, *Zeit. Kryst. Min.*, 1900, xxxii., 364). On halving the length c, and writing the axial ratios in orthorhombic form, the equivalence parameters are obtained as—

$$x : y : z = 3{\cdot}660 : 3{\cdot}583 : 3{\cdot}660.$$

These values approximate very closely to those obtained for picric acid, and indicate that the replacement of iodine in picryl iodide by hydroxyl, to yield picric acid, results in the corresponding assemblage being slightly expanded in all directions, in accordance with the second geometrical property described by Barlow and Pope (*Trans. Chem. Soc.*, 1907, xci., 1204).

The equivalence parameters determined above are collected in Table III.

An inspection of the equivalence parameters of those picryl derivatives which assume the hexagonal type of marshalling shows, as previously noted, that the substitution in the benzene assemblage occurs so that groups which enter the benzene assemblage as substituting radicles are accommodated as the result mainly of an expansion of the assemblage in the directions of x and y ; the z dimension of benzene can thus be distinctly traced throughout the series of picryl derivatives as the y dimension of the latter. This conclusion indicates that the columns, consisting of superposed layers of three triangularly arranged carbon spheres, which form the skeleton of the crystalline benzene assemblage (*Trans. Chem. Soc.*, 1906, lxxxix., 1695), exist in all these crystalline substances, and that the corresponding assemblages are derived by pushing these columns apart, and packing the substituting groups into the space thus provided. The equivalence parameters now given furnish the data requisite to the construction of diagrams, similar to those previously given by Barlow and Pope, which show the precise mutual arrangement of the constituents of the substituting radicles in the picryl derivatives.

If the conclusion drawn concerning the existence of the columns of carbon spheres in these assemblages is of general application, it should be possible to detect the z dimension for benzene throughout all the benzene derivatives of hexagonal marshalling.

No difficulty appears to exist in applying the method of treatment used in this paper to the more complex picryl derivatives. Thus, acetamide picrate, $CH_3.CO.NH_2,C_6H_2(NO_2)_3OH$, crystallises in the orthorhombic system with—

$$a : b : c = 0{\cdot}4849 : 1 : 0{\cdot}3544$$

(Wyrouboff, *Ann. Chim. Phys.*, 1895, [7], v., 99). The valency volume, W = 68, and the corresponding equivalence parameters are—

$$x : y : z = 3{\cdot}560 : 7{\cdot}342 : 2{\cdot}602.$$

Further, isoapiol picrate, $C_{12}H_{14}O_4,C_6H_2(NO_2)_3OH$, crystallises in the monosymmetric system with—

$$a : b : c = 0{\cdot}9163 : 1 : 0{\cdot}4226,\ \beta = 89^\circ\ 55'$$

(Boeris, *Zeit. Kryst Min.*, 1905, xl., 106). The valency volume, W = 120, and the corresponding equivalence parameters are—

$$x : y : z = 6{\cdot}201 : 6{\cdot}767 : 2{\cdot}860,\ \beta = 89^\circ\ 55'.$$

In each of these cases one of the three equivalence parameters has a value not greatly different from the value, $z = 2{\cdot}780$, for benzene: this would be expected if the columns of carbon spheres present in the benzene assemblage remain intact in these compounds.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

PART III.—ANALYSIS OF THE ALUMINIUM AND IRON GROUPS, INCLUDING BERYLLIUM, URANIUM, VANADIUM, TITANIUM, ZIRCONIUM, AND THALLIUM.

By ARTHUR A. NOYES, WILLIAM C. BRAY, and ELLWOOD B. SPEAR.

(Continued from p. 83).

**Procedure* 58*b*. — To the $NaHCO_3$ filtrate add HNO_3 (1·20) until the solution is distinctly acid, avoiding an excess of more than 1 cc. (Colourless solution, absence of *chromium*). Unless the solution is as colourless as pure water, test one-fourth of it for chromium by adding to the cold solution in a test-tube 2 cc. ether and 0·5—1·0 cc. 3 per cent H_2O_2 solution. (Blue coloration of the ether layer, presence of *chromium*). To this mixture add about 5 cc. HNO_3 (1·42). Red coloration of water layer, presence of *vanadium*).

If chromium is not present, treat the HNO_3 solution or the part of it not tested with H_2O_2 by *P. 58*c*.

If chromium is present, exactly neutralise the remainder of the HNO_3 solution with NaOH, add 2 cc. HNO_3 (1·20) and then 20 cc. 20 per cent $Pb(NO_3)_2$ solution; allow the mixture to stand for fifteen to twenty minutes, and filter. (Yellow precipitate, presence of *chromium*). Saturate the filtrate with H_2S, filter off and reject the precipitate; boil the filtrate for two or three minutes to expel H_2S and to coagulate any sulphur that may separate; filter off and reject the precipitate. In order to oxidise vanadyl salts to vanadate, add bromine water (or if much is required, liquid bromine) until the solution has a permanent reddish colour. Boil in a casserole until the bromine is expelled and treat the solution by *P. 58*c*.

Notes.

1. The $NaHCO_3$ filtrate should not be heated after acidifying because some H_2O_2 may still be present (even though most of it is decomposed in the heating with $NaHCO_3$), which would cause the reduction of chromate, and might thus prevent the detection of even several milligrms. of chromium. (See *P. 58*a*, N. 2).

2. It is desirable to determine in advance, by making a preliminary test if necessary, whether or not chromium is present, for, if it is absent, the addition of the lead salt and the subsequent removal of the lead with H_2S may be omitted. If lead be added, its removal is necessary before the tests for uranium and vanadium can be made. If the acid solution is perfectly colourless, an amount of chromium exceeding 0·5 mgrm. may safely be pronounced absent. Uranium and especially vanadium in moderate quantity (20 to 50 mgrms.) also give yellow solutions. A yellow solution is therefore tested for chromate with H_2O_2. In regard to this test, see P. 56, N. 1. The test can be made in only a small portion (one-fourth) of the solution, for it is so delicate that the presence of 0·1 mgrm. chromium in this portion can be detected. The portion in which the test is made is rejected, because chromium, if present, is reduced to the chromic state by the H_2O_2 in the acid solution, and would therefore not be precipitated by the lead nitrate.

3. When vanadium is present even in moderately small quantity, the water layer, on the addition of H_2O_2, becomes orange-yellow to orange-red in colour, owing to the formation of pervanadic acid. This test for vanadium becomes more delicate when the solution is made strongly acid as is directed; a distinct colour is then obtained even when only 0·5 mgrm. vanadium is present in the portion tested, corresponding to about 2 mgrms. in the whole solution. (Compare *P. 51*a*, N. 4). The test is not essential since vanadium is always tested for later; it is introduced here, where it can be made in a moment's time, as an additional confirmation of the presence or absence of that element.

4. The separation of chromium from vanadium and uranium by $Pb(NO_3)_2$ depends on the relatively small solubility of lead chromate in dilute HNO_3 in the presence of a large quantity of $Pb(NO_3)_2$. Under the conditions described in the procedure, over 100 mgrms. of vanadium yield no precipitate and only 0·1 to 0·3 mgrm. of chromium usually remains in solution, though this amount is somewhat increased when a very large quantity of $NaNO_3$ has been introduced. To secure these results, however, care must be taken to use the prescribed quantities of HNO_3 and $Pb(NO_3)_2$, for lead vanadate is also a difficultly soluble substance, and would be quantitatively precipitated in the presence of a much weaker acid, such as acetic acid in the presence of ammonium acetate. Lead uranate would also be precipitated from a neutral or slightly alkaline solution.

5. The presence of much chloride or sulphate would cause the precipitation of white $PbCl_2$ or $PbSO_4$, which might obscure the yellow colour of a small quantity of $PbCrO_4$ and prevent the estimation of the amount of chromium present. These anions will, however, not be present in harmful quantity, if in dissolving the original $(NH_4)_2S$ precipitate (P. 51) the acids are used in the way prescribed, and if in acidifying the solutions in *P. 58*a* and *b*, HNO_3 and not HCl is used, as directed.

6. The lead which is added to precipitate the chromate must be removed before testing for uranium with Na_2HPO_4 (in *P. 58*c*), since it would give a precipitate of $Pb_3(PO_4)_2$. It is precipitated with H_2S, rather than with $(NH_4)_2SO_4$, because in the latter case enough lead (about 1 mgrm.) still remains in solution to give a precipitate with Na_2HPO_4.

7. By the H_2S, vanadic acid is reduced to vanadyl nitrate $VO(NO_3)_2$ slowly in the cold but more rapidly on heating the solution, so that sulphur may be precipitated on boiling the filtrate to expel H_2S. This must be re-oxidised to vanadic acid, for otherwise vanadyl ammonium phosphate would be precipitated with the uranium phosphate in *P. 58*c*. The oxidation by bromine does not take place instantaneously; and a considerable excess of bromine must therefore be used, and the mixture allowed to stand for a few minutes.

**Procedure* 58*c*.—Make the solution obtained in *P. 58*b* neutral with NH_4OH, add 5 cc. 30 per cent acetic acid, 1—2 grms. solid $(NH_4)_2SO_4$ (or NH_4NO_3), and then 2 grms. solid $Na_2HPO_4.12H_2O$, and heat to boiling. (White precipitate, presence of *uranium*). Allow the mixture to stand ten to fifteen minutes to coagulate the precipitate, filter, and wash the precipitate with a 5—10 per cent solution of $(NH_4)_2SO_4$ (or NH_4NO_3). (Precipitate, *P. 58*d*; filtrate, *P. 58*e*).

* From the *Journal of the American Chemical Society*, xxx., No. 4.

Notes.

1. The precipitation of white uranyl ammonium phosphate, $UO_2NH_4PO_4$, is a delicate test provided the solution be made only moderately acid with acetic acid and a sufficient excess of Na_2HPO_4 be added. The separation from vanadium as vanadic acid is a very satisfactory one, for vanadium, even when present in large quantity (100 mgrms.), does not precipitate, nor is a small quantity carried down by uranium; on the other hand, 0·5 mgrm. uranium gives a distinct precipitate. The test is a somewhat more delicate one if made in a smaller volume, say 40 cc.; in this case the same quantities of reagents may still be used, and the separation is perfectly satisfactory.

2. The formation of a precipitate at this point is not sufficient evidence of the presence of uranium, for aluminium, beryllium, and lead will separate as phosphates if they have not been completely removed in previous procedures, and vanadium will precipitate as vanadyl ammonium phosphate if the oxidation by bromine was incomplete. On the other hand, a slight turbidity may correspond to an appreciable amount of uranium (0·2 to 0·5 mgrm.). Therefore the confirmatory test for uranium (*P. 58*d*) should always be tried.

3. When the solution is made alkaline with NH_4OH a pale yellow precipitate of uranyl ammonium vanadate may separate, and may not dissolve when the acetic acid is added. This, however, has no effect on the separation, since, on boiling, it is converted into the less soluble uranyl ammonium phosphate and vanadic acid.

4. In the absence of ammonium salts uranium is precipitated as uranyl hydrogen phosphate, UO_2HPO_4, which often separates as a very finely divided precipitate that runs through the filter. The ammonium salt is added to cause the uranium to precipitate as uranyl ammonium phosphate, which coagulates and filters more readily.

**Procedure* 58*d*. — Dissolve the Na_2HPO_4 precipitate (*P. 58*c*) by pouring a small portion of hot HCl (1·12) repeatedly through the filter, evaporate the solution nearly to dryness, add about 10 cc. nearly saturated NaCl solution, pour into a test-tube, cool, and add 5 cc. 10 per cent $K_4Fe(CN)_6$ solution. (Dark red precipitate or coloration, presence of *uranium*).

Notes.

1. The precipitation of the dark red uranyl ferrocyanide $(UO_2)_2Fe(CN)_6$ is a very characteristic and also a very delicate test for uranium, provided care be taken to avoid any excess of acid. The solution must, however, be distinctly acid, for otherwise the precipitate may not form, owing to the small concentration of the uranyl ion, $UO_2{+}{+}$. Uranyl ferrocyanide tends to form a colloidal solution; but the presence of NaCl and HCl soon causes it to coagulate.

Procedure 58*e*.—Neutralise the filtrate from the Na_2HPO_4 precipitate (*P. 58*c*) with NH_4OH (0·90) and add at least 5 cc. more. Saturate the solution completely with H_2S by passing the gas through it in a small flask for ten or fifteen minutes. (Pink or violet red colour, presence of *vanadium*). Pour the solution through a filter; make it distinctly acid with acetic acid (or HCl) and heat nearly to boiling. (Dark precipitate, presence of *vanadium*).

Notes.

1. In regard to the formation of the sulphovanadate of vanadium in the strongly alkaline solution, the partial precipitation of vanadium sulphide on acidifying, and the action of H_2O_2 on vanadic acid, see the Notes on *P. 51*a*.

Procedure 58*f*.—Heat the $NaHCO_3$ precipitate (*P. 58*a*) with 10—30 cc. HCl (1·06) in a casserole, or dissolve it by pouring the acid two or three times through the filter, boil the solution to expel CO_2, add NH_4OH (0·96) until the solution after shaking smells of it, and then 2—3 cc. in excess. Heat the mixture nearly to boiling, filter and wash the precipitate, using suction if it seems desirable. (Precipitate, *P. 58*g*; filtrate, acidify with acetic acid and test for zinc by P. 57).

Notes.

1. The zinc remains in the ammoniacal filtrate as a complex ammonia salt, chiefly $Zn(NH_3)_4{+}{+}Cl_2{-}$. Aluminium and beryllium are precipitated as hydroxides. The precipitate will also contain any uranyl vanadate that was precipitated in the $NaHCO_3$ separation.

**Procedure* 58*g*. — Dissolve the NH_4OH precipitate (*P. 58*f*) by pouring a hot 5—15 cc. portion of HCl (1·12) repeatedly through the filter, using another portion of acid, if necessary. Add a volume of ether equal to one and a-half times that of the solution. Pass into the mixture in a small flask HCl gas until a single layer results, and until fumes of HCl are copiously evolved, cooling the flask in running water during the progress. Cover the flask and let the mixture stand for fifteen minutes even if no precipitate has separated. (White crystalline precipitate, presence of *aluminium*). Filter through an asbestos filter (see P. 61) or an ordinary filter supported by a small hardened filter folded with it, after first moistening the filter with a mixture of two volumes of HCl (1·20) and three of ether previously saturated with HCl gas; wash the precipitate once with this mixture. During the filtration and washing keep the funnel covered with a watch-glass to prevent evaporation of the ether. (Precipitate, P. 54, to confirm presence of aluminium; filtrate, *P. 58*h*).

Notes.

1. Aluminium chloride, $AlCl_3.6H_2O$, is only slightly soluble in concentrated HCl solutions and the precipitate is complete when ether is added and the mixture saturated with HCl. 0·5 mgrm. of aluminium can be easily detected in 30 cc. The test is therefore a delicate one. It is also very characteristic; for no other element of the aluminium group is precipitated by this treatment, except chromium when it is present in moderate quantity.

2. The ethereal solution of HCl, unlike the concentrated aqueous solution, does not disintegrate filter-paper rapidly, and the filtration can almost always be made with an ordinary filter supported by means of a hardened filter. This filtration is apt to be slow, and it is often advantageous to filter through asbestos with the help of suction.

3. When the NH_4OH precipitate is small (corresponding to less than 30 mgrms. Al), it need not be treated by this procedure, but it may be dissolved in a little HCl, and treated directly by *P. 58*h*.

**Procedure* 58*h*.— Evaporate the filtrate from the HCl precipitate (*P. 58*g*), first on a water-bath under a hood until the ether is expelled, and then over a flame, almost to dryness until nearly all the HCl is expelled; add a little water, make alkaline with NH_4OH, avoiding a large excess, and heat nearly to boiling. (No precipitate, absence of *beryllium*).

If there is a precipitate, dilute to 30 cc., add enough solid $NaHCO_3$ to make a 10 per cent solution, heat to boiling, boil for one minute, cool, pass in H_2S for a few seconds, and filter after a few minutes if there is a precipitate. Acidify the filtrate with HCl, boil for two or three minutes to expel CO_2, make the solution alkaline with NH_4OH, and heat nearly to boiling. (White flocculent precipitate, presence of *beryllium*; yellow precipitate, presence of *uranium*).

Treat this precipitate or a portion of it corresponding to about 20 mgrms. of beryllium by *P. 58*d*. (Dark red precipitate, presence of *uranium*). Filter, and to the filtrate add NH_4OH. (White precipitate, presence of *beryllium*).

Notes.

1. The filtrate from the HCl precipitate may contain besides beryllium, uranium or vanadium (carried down in the treatment with dilute $NaHCO_3$ in *P. 58*a*), aluminium (if care was not taken in precipitating and filtering aluminium chloride), and a little iron (introduced from the reagents). This solution is first tested with NH_4OH to determine if any further treatment is necessary. The treatment with the hot concentrated $NaHCO_3$ solution serves to precipitate the aluminium completely and to dissolve the beryllium and uranium. This method of separation of aluminium and beryllium is a satisfactory one, when, as in the present case, only a small amount of aluminium is present; a large quantity of aluminium, however, retains almost completely a small quantity of beryllium. The $NaHCO_3$ solution must not be boiled for a long time, because, owing to the escape of CO_2 and the formation of free NaOH, the solution becomes alkaline enough to dissolve some aluminium. The reason for the great solubility of beryllium hydroxide in concentrated $NaHCO_3$ solutions is not known. H_2S is passed in to remove the iron, since a small amount of it remains dissolved in the concentrated $NaHCO_3$ solution; the filtrate is sometimes dark green even after repeated filtration, due to the presence of colloidal iron sulphide; to precipitate this, add a small amount of a ferrous salt (say 2 to 4 mgrms. Fe), shake, allow the mixture to stand several minutes, and then filter, finally passing more H_2S into the filtrate to make sure that the iron has been all removed.

2. The treatment with $K_4Fe(CN)_6$ described in *P. 58*d* gives a satisfactory separation of beryllium from uranium (and vanadium) provided the amount of beryllium in the solution does not exceed 20 milligrms. When more beryllium is present a gelatinous precipitate separates; on this account it is directed to use only a portion of the NH_4OH precipitate when it is large, but even in this case a small amount of uranium can still be detected, owing to the delicacy of the ferrocyanide test. Vanadium, if present owing to its having been precipitated as uranyl vanadate in the treatment with dilute $NaHCO_3$ (*P. 58*a*), remains with uranium and is precipitated as greenish yellow vanadyl ferrocyanide, but does not obscure the dark red colour of the uranium precipitate. It is not necessary to provide for the detection of vanadium at this point, since a large quantity always dissolves in the $NaHCO_3$ treatment.

(To be continued).

NOTICES OF BOOKS.

Matriculation Directory. June, 1908. London: University Tutorial Press, Limited. 1908.

This Directory to the Matriculation Examination of the University of London will be particularly useful to those students who are endeavouring to prepare themselves for the examination without the assistance of a tutor. It contains the papers set in the June examination with full solutions and criticisms of many of them, and the introduction makes valuable suggestions as to the most suitable text-books for the students' use. The advice given is, on the whole, sound, and the books recommended are undoubtedly reliable for the special purpose in view, although in many cases their value as general educational instruments may be inferior to that of others which have not been written so exclusively to meet the requirements of one particular syllabus.

The Theory of Ions. By William Tibbles, M.D., &c. London: Rebman, Limited. 1908.

This little book is a rather skilfully worked up summary of modern theories relating to the applications of physica chemistry to physiological problems, which of recent years have been made the subject of thorough investigation by many observers. The author's treatment of these problems contains nothing essentially new, nor is it even clear upon what definite facts he bases his opinion that life is a gradual development of an evolutionary character from dead to living matter, and that ions are the intermediate substance between living and non-living matter. However, the theories of physical chemistry are clearly stated in simple language, and the book will be interesting reading for those who take pleasure in studies of the origin of life and kindred problems.

CORRESPONDENCE.

MUST WOMEN BE DENIED FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

Sir,—It is disturbing to learn, from his letter in the Chemical News of July 31st, that Mr. Droop Richmond did not mean what he set his hand to in the Petition concerning the Fellowship of the Chemical Society, namely, that he was "of opinion that the time had come when the Fellowship of the Society should be rendered accessible to women." More than this, to sign, as he explains he did, only to ascertain the wishes of the Society as to the admission of women, would seem to most people to be an unwarrantable act of aimless curiosity on the part of one who did not want to have them admitted. Let us hope, therefore, that Mr. Richmond may be wrong in believing himself to be not the only Fellow who signed as he did.

If Mr. Droop Richmond will refer to my letter of July 17th, he will see in it that I took no side on the question of admitting women to the Fellowship, and that, therefore, I could not, as he asserts, have given away one side or the other. He will further see that the whole of my letter was devoted to the endeavour (successful, I think) to show that, inadvertently, the procedure of the last Meeting of Council of the Society, acted upon in the way it was in the letter of the Honorary Secretaries, was calculated to affect unfavourably the success of the object of the petition. Mr. Richmond appears to have mistaken my position. For, I hold, not only that it is fair and proper, but that, in the interests of the Society and of chemistry, it is the duty of every Fellow to vote and to do all that he legitimately can to persuade others to vote his way on this matter of the admission of women. Acting upon this conviction, I wish now, sir, to be allowed to meet (what it was not my purpose to do in my first letter) the objections raised against granting the Fellowship to women.

The arguments for opening the Society to women are well stated in the Petition and in the Honorary Secretaries' letter, and such attempts as have been made to meet them do not seem to be serious enough to call for reply here. The real opposition to the admission of women has taken the form of arguments considered to outweigh in importance all that can be said in favour of admitting them. What appears to be the principal of these is put in the following paragraph.

The Fellowship of the Chemical Society would be an aid to a woman in getting employment as a chemist. Consequently, the possibility of gaining entrance to the Society on equal terms with men would encourage women to choose chemistry as the means of a living. But women ought not to be thus encouraged, because, not only is the work of the chemist of too arduous a nature for them, but they might on equal terms successfully compete for remunerative employment with men, many of whom support, or would support, a wife and children out of their earnings as chemists.

To me this argument is quite beside the mark, and, if it

were not, would still be indefensible, as I proceed to explain. It is beside the mark, since the object of the Society is the general advancement of chemical science. Such it is said to be expressly in the Charter, and such is what it has always been in the practice of the Society. Many times in past years, to learn that a candidate sought the right to append the letters F.C.S. to his name for "professional pursuits" or purposes led the voting Fellows to blackball him. It was, too, because the Society could not take up the professional interests of chemists that the Institute of Chemistry was founded. That Institute, by the way, whilst doing inestimably good service in looking after these interests, has not found it to be part of its duty to inquire into the sex of the candidate for its diploma.

The Chemical Society has no power under its Charter to issue in the form of its Fellowship, or in any other way, an authorisation to engage in chemical work, or a declaration of the competence of any one to engage in it. It has, therefore, had no consideration at all when granting its Fellowship, and can have none, for the question whether a candidate will be too feeble for "the arduous nature of chemical work." It has no consideration, either, for the question whether additional Fellows "may . . . find employment in view of the already overcrowded state of the profession," or whether its Fellowship must be restricted to those who have already, or are looking to have, a wife and children. It is utter silliness and rank trades-unionism to suggest that it has. The interests of the Society lie wholly in the advancement of chemical knowledge, and the welfare of the Society is measured by its success in this work, as shown by the ratio of increase in the number of its Fellows : *Multi pertransibunt et augebitur Scientia.*

This being so beyond disputes, it is to me an insolvable problem how a Fellow can believe it to be honourable and loyal to the Obligation he has signed to try to prevent a woman being a means, by becoming a Fellow, of "promoting the interests and welfare of the Society," in order thereby to impede her in a possible competition with himself, or some other man chemist, for a living. A Fellow has to vote as such and in no other capacity, and to be true to the interests of the Society, whatever he may deem to be his private interests.

Having, however, to face the fact that there are Fellows who are ready to put personal advancement before public responsibilities, I would point out to them, since they do recognise the claims of women to admission and express sorrow (some of them) at having to try to keep them out, that at the worst for themselves, it must be very many years before the competition of women for employment as chemists will be more than that of one woman against hundreds of men ; that it is the F.I.C. and the D.Sc., and not the F.C.S., which help chemists, women as well as men, to get appointments. The success already of women, even without the F.C.S., may be used against my argument that women chemists will for long be too few to be feared. But that is a dangerous objection to raise. I have special opportunity for judging and knowing about some University appointments filled by women chemists, and I am convinced that the interests of the Universities concerned would not be better served by replacing these chemists by men. Then, if I am right, what is the use of striving to keep women out of employment as chemists by handicapping them in their competition with F.C.S.'s ?

An argument advanced by Mr. Richmond against admitting women to the Fellowship is that they will be favoured on account of their sex by those estimating their fitness for it and the value of their papers. Supposing this to be true, the argument would only hold good were the F.C.S. a certificate of merit and ability, and it falls far short of being that. Moreover, the great majority of the present Fellows have no papers of theirs in the *Transactions* of the Society. Whilst, however, I do not see that the argument justifies Mr. Richmond in voting and asking others to vote against the admission of women into the Society, I admit that there is something in his objection to a woman chemist getting an unfair advantage in competition by means of exaggerated representations as to her chemical ability because of her sex. We may, however, count upon this abuse, if it exists, working out its own cure, and in the meantime we may war against it where we meet with it. Women themselves now cry out for no favour for sex, which is wise of them, and I am sure they mean it.

A more certain grievance for some men chemists against women chemists is that owing (not to the over-estimation, but) to the under-estimation of the value of women's abilities women may, and already do, have to render equivalent services for less pay than men chemists receive. Helplessly they may thus become unfair competitors with men. But this, of course, is a matter quite independent of that of the Fellowship.

The argument that the quantity of women's chemical work is insignificant when compared with that of the men is another having no application to the question of admitting women into the Society. Let there be but one woman waiting for admission whose chemical ability is beyond dispute, or even one who in the opinion of half-a-dozen Fellows signing her certificate, and that of the necessary majority at a meeting voting for her, why should she be forbidden the Fellowship because of there being, by supposition, not much in favour of other women ?

Yet another argument against women getting the Fellowship is that it would then be possible for a woman to become a Member of Council or other Honorary officer (there is, of course, already that admirably efficient, paid officer, Mrs. Dougal). Again, it has to be said, this is no just or allowable ground for excluding women. It is, besides, highly improbable that a woman Fellow would get office unless eminently qualified for it, but who then could object ? Her sex certainly would be no qualification for office. It is unreasonable to suggest that women, as a sex, will ever prove themselves to be better chemists than men, but unless they do there can be no chance of predominance of women in the Chemical Society.

I have, lastly, to refer to the difficulty in the way of letting women into the Society caused by the wording of the Charter, which is ambiguous. In the By-law on the election of a Fellow the candidate is spoken of as "he." Does this pronoun really signify here the sex of the candidate ? It is a familiar fact that the masculine pronoun is not only used for a male but for any member of the species, man, when the notion and distinction of sex are not involved. There were no women chemists when the Charter was granted, and no one will now contend that the pronoun was meant to be exclusive of women—that one condition of Fellowship was that the candidate must be male and not female. Provided that the Fellows as a body should not object, there would be no difficulty on this point, and "he" would be taken in its personal non-sexual sense. At worst, however, a Supplementary Charter, introducing only the additional words "or she," may be necessary, and an amended Charter is wanted on other grounds.

In conclusion, I venture to assert, as proved, that there is not one well-founded argument against the admission of women to the Fellowship of the Chemical Society, whatever may be the value of the trades-unionist arguments for persuading women not to attempt the practice of chemistry as a living, arguments, be it added, which apply equally to any more men who think of doing so.—Yours, &c.,

Edward Divers.

London, August 10, 1908.

CITRIC ACID.

To the Editor of the Chemical News.

Sir,—I should be glad if you could favour me with the whole or part of the following information on the production of citric acid desired by the Italian Government :—

1. List of firms in England using citrate of lime to produce citric acid, citrate of iron, and other products derived from citric acid.

2. Statistics of the annual importation into England of citrate of lime (Italian) from the various countries of origin for at least ten years.

3. The general contract conditions in buying citrate of lime (Italian) by English firms.

4. Half-yearly average prices of citric acid and of citrate of lime, and also average price for a period of ten years (Clause "C.I.F." and "F.O.B.," as the case may be).

5. Cost of production of 100 kgrms. of citric acid made with citrate of lime in England.

6. Purposes for which the products derived from citrate of lime in England are used, and quantity disposed of in England of such products.

7. List of importers of citrate of lime, concentrated juice, and raw juice.—I am, &c.,

L. ALLATINI,
Italian Consul General.

NITRIC ACID.

To the Editor of the Chemical News.

SIR,—For a small work I have in hand I wish to obtain the following particulars. Could you very kindly assist me to get them (or some) either by giving the figures or by saying where I could get them myself?

1. (*a*) Number of plants in Great Britain for making nitric acid. (*b*) Output —, total —, or for each if possible.

2. (*a*) Number of plants in Great Britain for making explosives which require nitric acid. (*b*) Tons of acid required if they were working normal full capacity.

3. (*a*) The different kinds of industrial uses for nitric acid. (*b*) Average amount they require (each kind of business) annually.

4. (*a*) Tons of nitric acid imported annually; (*b*) exported.—I am, &c.,

E. J. DEASON.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. cxlvii., No. 2, July 13, 1908.

Action of Metallic Oxides (Irreducible) on Primary Alcohols.—Paul Sabatier and A. Mailhe.—Some metallic oxides which are not reducible act as catalytic decomposition agents upon primary alcohols at temperatures below 360°. Certain oxides, *e.g.*, manganous oxide, stannous oxide, decompose the alcohols, setting hydrogen free. Other oxides, *e.g.*, alumina and thoria, dehydrate alcohols; thus with ethyl alcohol they give ethylene, and some aldehyde condensation occurs; others give rise to both reactions simultaneously. The proportion of the two reactions varies according to the nature of the oxide and the temperature. The effect of raising the temperature is to increase the velocity of the two reactions, especially that of the aldehyde condensation.

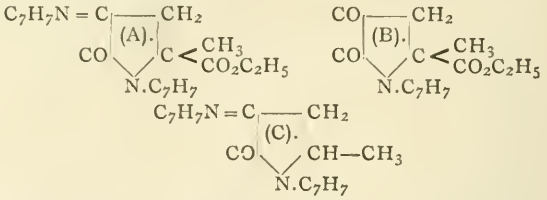
Mechanism of Synthesis of Nitrogen Cycles. Action of Ethyl Pyruvate on Paratoluidine.—L. J. Simon.—The action of ethyl pyruvate on paratoluidine may be represented by the equation—

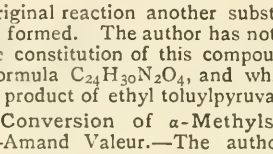
$$CH_3\text{--}CO\text{—}CO_2C_2H_5 + 2C_7H_7\text{—}NH_2 = C_{22}H_{24}N_2O_3 + C_2H_5OH + 2H_2O.$$

$C_{22}H_{24}N_2O_3$ may be called A. Sulphuric acid causes the elimination of one molecule of paratoluidine — $C_{22}H_{24}N_2O_3 + H_2O = C_{15}H_{15}NO_4 + C_7H_7NH_2$. This new substance B is distinguished from A by its enol and ketone properties. With alcoholic potash A is saponified, yielding a third substance C.

$$C_{22}H_{24}N_2O_3 + 2KOH = C_{19}H_{20}N_2O + CO_3K_2 + C_2H_5OH.$$

The formulæ of these three substances A, B, and C are—





By the same original reaction another substance differing from A may be formed. The author has not yet definitely determined the constitution of this compound, which has the empirical formula $C_{24}H_{30}N_2O_4$, and which may be a polymerisation product of ethyl toluylpyruvate.

Sparteïn. Conversion of α-Methylsparteïn into Isosparteïn.—Amand Valeur.—The author has shown experimentally that by boiling a solution of α-methylsparteïn in dilute sulphuric acid until potassium permanganate is only very slightly reduced, and adding barium iodide, the sulphate of α-methylsparteïn isomerises, giving isosparteïn sulphomethylate, which can be isolated by slow evaporation *in vacuo*. The analogy between sparteïn and N-methylpiperidine is complete. N-methylpiperidine when subjected to Hofmann's reaction is transformed into an unsaturated base, N-dimethylpiperidine, the chlorhydrate of which forms the cyclic compound dimethylpyrrolidine chlormethylate; the ammonium hydrate corresponding to this last salt is decomposed, regenerating N-dimethylpiperidine. Similarly sparteïn by reactions of the same type yields α-methylsparteïn, isosparteïn, iodomethylate, and (by Hofmann's method) α-methylsparteïn.

Researches on Acid Sulphates of Potassium.—L. Arzalier.—The existence of the compound $SO_4K_2.\frac{3}{2}SO_4H_2$ cannot be proved by thermic methods. The amount of heat set free by the fixation of $\frac{3}{2}H_2SO_4$ to SO_4H_2 should be greater than $\frac{3}{4}$ of the amount of heat set free by the fixation of one molecule of sulphuric acid, whereas it is slightly smaller. This compound is formed only in the hydrated state in the presence of water, owing to the heat of hydration (+5·383). It seems *a priori* impossible that a more acid compound than $SO_4K_2.3SO_4H_2$ could exist, for the molecules of sulphuric acid which would add themselves on would have to set free less than 2·42 cals., which represents the heat of fixation of one molecule of sulphuric acid to the acid sulphate $SO_4K_2.SO_4H_2$. The substance thus obtained would be very unstable.

Analysis of Wines.—Paul Dutoit and Marcel Duboux.—By neutralising and measuring the electrical conductivity of the solution it is possible to determine simultaneously the sulphates, the total acidity, and the tanning matter in wine. A concentrated solution of alkali is added to the wine in small portions, and the conductivity is determined after each addition. The graphic representation of the values thus obtained gives a curve which is characteristic of each wine and each alkali. When baryta is used as alkali the curve assumes a definite form, and from the lengths of certain parts of the curve it is possible to determine accurately the constituents of the wine.

"Patents and Designs."—A new illustrated weekly journal with this title will be published at 5, Tavistock Street, Strand, London, W.C., on the 22nd inst., by Mr. F. H. Pedgrift, whose name has been so long associated with successful newspaper management. This paper is called into existence by the coming into force on the 28th inst. of the principal provision of the new Patents Act, which will practically revolutionise existing relations between foreign patentees and British manufacturers. The price of the paper will be twopence.

THE CHEMICAL NEWS.

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ON THE ATOMIC WEIGHT OF CHLORINE.*

By EDWARD C. EDGAR, D.Sc., Assistant Lecturer in Chemistry in the University of Manchester.

Six years ago Prof. Dixon and I began a research with the object of determining directly the weight of chlorine which combines with the unit weight of hydrogen. Our method was to burn a jet of hydrogen in an atmosphere of chlorine; hydrogen being stored and weighed in palladium, the chlorine being condensed and weighed as liquid. The number we obtained for the combining weight of chlorine was appreciably higher than that found indirectly by Stas, and still higher than that approved by the International Committee on Atomic Weights.

While this research was in progress, other determinations had been made bearing on the relative weights of silver, chlorine, and nitrogen, so that some modification in the accepted values of one or more of these elements appeared inevitable. The direct "joining up" of the two ends of the chain connecting hydrogen with chlorine thus became a matter of immediate importance. Since the method of burning one gas in an atmosphere of the other had been proved to be accurate within fairly narrow limits, I was encouraged to continue the investigation, and to modify the apparatus, with a view to eliminate some of the possible sources of error in the former series of experiments.

The most important source of error lies in the weighing of the hydrogen. To diminish this error the weight of hydrogen employed was doubled; and since Prof. Dixon and I found, when water was used to condense the hydrogen chloride formed in the flame, that some of the water vapour was decomposed by the free chlorine, I avoided this by burning a jet of chlorine in dry hydrogen, condensing the hydrogen chloride as it was formed in a tube dipped into liquid air. In some of the experiments the hydrogen chloride formed has been weighed. My experiments (concluded in 1907) agree closely with the results previously obtained in 1905. The method employed was briefly as follows:—

Hydrogen, made by the electrolysis of barium hydrate solution, and dried by potash and phosphorus pentoxide, was occluded, and weighed in palladium contained in a boro-silicate glass bulb. The chlorine, prepared by electrolysing fused silver chloride in a Jena glass vessel, was weighed as a liquid in a thick-walled boro-silicate glass bulb. Two ground joints attached these bulbs to a quartz combustion vessel, which was also connected with a vertical quartz tube, and with a steel bomb and a pump. After a thorough evacuation of the whole apparatus, the vertical limb of the combustion vessel was immersed in liquid air. Then the vacuous vessel was filled with hydrogen from the heated palladium bulb. Chlorine was ignited by a spark at the tip of a quartz jet, and continued to burn in the atmosphere of hydrogen with a fine needle-shaped flame. The endeavour was made so to regulate the gases as to maintain the flame until nearly all the chlorine weighed had been burnt. Then the supply of hydrogen was cut off. As the atmosphere became more attenuated the flame died away until, just before it went out, the chlorine was turned off. The hydrogen chloride, immediately after it was formed in the flame, was condensed as a snow-white solid by the liquid air surrounding the vertical limb of the combustion vessel; and a little chlorine, which had escaped burning, was also solidified. At the end of the combustion, the residual gas was extracted by the pump and analysed; it proved to be practically pure hydrogen.

Then the snow-white hydrogen chloride was allowed to evaporate. By passing the gas through a quartz tube filled with mercury vapour, the chlorine it contained was completely removed, and the purified hydrogen chloride passed on to a steel bomb immersed in liquid air, where it was condensed in six experiments, and successfully weighed in three; in the other three the bomb leaked. In two other experiments the gas was absorbed by water, and weighed as aqueous acid. The weights of hydrogen and chlorine burnt were obtained by subtracting from the total weight of each used the weight of hydrogen extracted by the pump, and the weight of chlorine caught by mercury vapour respectively.

The balance was specially made for this work by Oertling; even under the load of the steel bomb, weighing over 1000 grms., it gave very reliable readings. Each piece of apparatus weighed was tared with another of the same material, and of very nearly equal volume and weight, and the small weights used in the weighings were reduced to a vacuum standard.

	Hydrogen burnt, in grms.	Chlorine burnt, in grms.	Hydrogen chloride caught, in grms.	$\frac{\text{Chloride burnt}}{\text{Hydrogen burnt}}$.	$\frac{\text{Hydrogen chloride caught} - \text{hydrogen burnt}}{\text{Hydrogen burnt}}$.
1.	2·1452	75·5026	77·6469	35·196	35·196
2.	2·0387	71·7504	73·7880	35·194	35·194
3.	1·7762	62·5004	—	35·188	
4.	1·9935	70·1638	72·1565	35·196	35·196
5.	1·6469	57·9671	—	35·198	
6.	2·1016	73·9662	—	35·195	
7.	1·7254	60·7162	62·4401	35·190	35·189
8.	2·0885	73·4991	75·5859	35·192	35·191
			Mean	35·194 ± 0·0008	35·193 ± 0·0009

Above are set out the corrected weights of hydrogen and chlorine burnt in eight experiments, and the weights of hydrogen chloride caught in five.

If the atomic weight of hydrogen be taken as 1·00762, the mean values for the atomic weight of chlorine, calculated from the numbers in the accompanying table, are 35·462 ± 0·0008 and 35·461 ± 0·0009.

Dixon and Edgar, burning hydrogen in chlorine, found the equivalent of chlorine to be 35·463 ± 0·0019 from their nine experiments.

The concordance of the two sets of experiments is thus exceedingly close, and the number 35·462 may be taken as representing the result of the whole work.

On the other hand, Noyes and Weber (*Journ. Am. Chem. Soc.*, 1908, xxx., 13), by passing a known weight of hydrogen over weighed potassium chlorplatinate, noting the loss in weight of the salt, and condensing and weighing in water the hydrogen chloride formed, have recently obtained for the atomic weight of chlorine the mean number 35·452 ± 0·0008 (H = 1·00762).

In view of the promised re-calculation of the atomic

* Abstract of a Paper read before the Royal Society, June 25, 1908.

weights by the International Committee this year, I have not attempted to correlate my results with the recent determinations of silver, nitrogen, and chlorine.

THE ELECTROLYTIC PROPERTIES OF DILUTE SOLUTIONS OF SULPHURIC ACID.*

By W. C. D. WHETHAM, M.A. F.R.S., and H. H. PAINE, B.A., Trinity College, Cambridge.

PART I.—*By* W. C. D. WHETHAM.

1. *The Electrical Conductivities.*

THE first section of the present paper contains an account of a continuation of the work described in the *Proceedings of the Royal Society* (1905, A, lxxvi., 577), and a statement of the object of the investigation may be reproduced from that place :—

"If the measure of the electrical conductivity of a solution be divided by that of the concentration expressed in gramme-equivalents per unit volume, we obtain a quantity which may be called the equivalent conductivity of the solution. If the conductivity of the solvent used be subtracted from that of the solution, the corresponding quantity may be taken as giving the equivalent conductivity of the solute.

"As is well known, the equivalent conductivity of neutral salts, when dissolved in water, approaches a limiting value as the dilution is increased, and, in terms of the ionisation theory, this limiting value corresponds with complete ionisation.

"With solutions of acids and alkalis, however, the phenomena are different. As dilution proceeds, the equivalent conductivity reaches a maximum at a concentration of about a one-thousandth or a two-thousandth of a gramme-equivalent per litre, and then falls rapidly as the dilution is pushed farther.

"It has been supposed that this diminution of equivalent conductivity at extreme dilutions is due to interaction between the solute and the impurities which remain even in re-distilled water.

"Kohlrausch has given evidence to show that the chief impurity in water carefully re-distilled is carbonic acid," but the experiments described in the writer's former paper show that no appreciable change in the phenomenon is produced by boiling the water used as solvent repeatedly under low pressure, and re-admitting the air through potash bulbs. This process would remove a great part at least of the carbonic acid in the solvent, and it causes a large diminution in the conductivity of the water, but, on adding small quantities of sulphuric acid to solvent so purified, a conductivity curve of the normal type is obtained—the lowering of equivalent conductivity at great dilution is not affected appreciably. The first step in continuing the research consisted in repeating the process of boiling the solvent under diminished pressure, but in re-admitting air through bulbs containing dilute sulphuric acid as well as others containing potash. Any volatile alkaline impurity such as ammonia would thus partly be removed, and if such impurity were the cause of the phenomenon, the conductivity curves obtained by adding acid to the purified solvent would be modified. The results obtained are given in Table I.

As comparative numbers only were needed, the conductivities were expressed in arbitrary units—the reciprocals of the measured resistances in the cell employed. It will be seen that the usual phenomenon of a fall in the equivalent conductivity at great dilution is still evident, and the curve obtained by plotting $m\lambda$ and k_0/m is not appreciably different from that obtained when unboiled distilled water is used as solvent.

Thus the efforts made to remove residual ammonia are without result on the conductivity of solutions of sulphuric acid made up with the solvent so purified.

* A Paper read before the Royal Society, June 18, 1908.

Hence it seems that traces in the solvent neither of carbonic acid nor ammonia are competent to explain the peculiarities in the conductivity of dilute solutions of acids. As will be pointed out in Part II. of this paper, however, another possibility remains, namely, the presence in re-distilled water of traces of carbonate or bicarbonate of ammonia. Such an impurity might produce the effect observed both with acids and with alkalis, and the slight trace of it requisite might not be removed by treatment such as is described above. However this may be, it seems unlikely that the impurity which is usually assumed to be the cause of the phenomenon is competent to explain it.

2. *The Transport Ratios.*

If the phenomenon of the decrease in equivalent conductivity be not due to impurities in the solvent, it must be caused by some change in the conductivity of the solute itself. A decrease in conductivity must be accompanied by a decrease in the effective velocity of one or both of the ions. Since the phenomenon under investigation occurs with alkalis as well as acids, it seems likely that, if it be not due to impurities, it depends on the presence of the one ion in each of these classes of compounds which is identical with one of the ions of the solvent—in acids the hydrogen ion, and in alkalis the hydroxyl ion. Hence, on the supposition we are now making, it is probable that one ion would be affected in a different way to the other. We may expect that in solutions of acids, the hydrogen ion travels slower at great dilutions than at more moderate concentrations. Such a differential treatment of the ions would be made manifest by a determination of the migration constant or transport ratio of solutions of different concentrations. If an electric current be passed through a solution between non-dissolvable electrodes, solute is lost from the solution in the neighbourhood of both electrodes, and it is readily shown that the ratio of loss is equal to the ratio between the opposite ionic velocities. The ratio of the velocity of the anion to the sum of the velocities is taken as the transport ratio or migration constant. A decrease in the velocity of the hydrogen ion of acids, then, would cause an increase in the measured transport ratio.

The transport ratio usually has been measured by determining the concentration of the solution by chemical means before and after the passage of the current in the neighbourhood of the two electrodes. But, in the present case, the concentrations involved were far too small to be estimated chemically; it was necessary to devise a new method.

Now, in the measurement of electrical conductivity, we possess a means of determining the concentration of a dilute solution much more sensitive and accurate than any method of chemical analysis, and a method of experimenting was designed to utilise these advantages.

Fig. 1 shows a cell made of Jena glass. It consists of two vertical tubes connected horizontally through an inverted V, to the apex of which a quill tube of glass is fused. To this quill tube is fixed a piece of rubber tubing, and by a slight increase of air pressure the level of the liquid in the inverted V can be depressed so as to separate the liquid into two parts, one confined to each vertical limb of the apparatus.

In each vertical tube are placed two platinum electrodes, carried by glass tubes through the ends of which stout platinum wires are sealed. By measuring the resistance between these electrodes, the specific resistance of the solution round them can be determined, while, if each pair of electrodes is connected electrically together, a current may be passed through the whole apparatus from one pair of electrodes to the other when the liquid fills the inverted V tube as well as the vertical limbs.

The electrodes in the side tubes lie just above the junctions with the connecting tube. By this arrangement, the danger of convection currents, leading to a mixture of the anode and cathode portions of the solution, is avoided, for, in the cathode region, where the concentration diminishes, the lighter liquid rises towards the surface, while the denser anode liquid has no tendency to pass into

TABLE I.

No. of solution.	Concentration (grm.-equivalents per 1000 grms. of solution = m.	$m^{\frac{1}{2}}$.	Conductivity at 18° C. in arbitrary units = k.	Conductivity less that of solvent = k_0.	Equivalent conductivity of sulphuric acid = k_0/m.
0.	0·0	—	$1·041 \times 10^{-5}$	—	—
1.	$4·812 \times 10^{-5}$	0·03638	$1·800 \times 10^{-4}$	$1·696 \times 10^{-}$	3·526
2.	$9·158 \times 10^{-5}$	0·04506	$3·542 \times 10^{-4}$	$3·438 \times 10^{-4}$	3·757
3.	$1·983 \times 10^{-4}$	0·05831	$7·817 \times 10^{-4}$	$7·713 \times 10^{-4}$	3·890
4.	$3·579 \times 10^{-4}$	0·0710	$1·413 \times 10^{-3}$	$1·403 \times 10^{-3}$	3·936
5.	$6·523 \times 10^{-4}$	0·0935	$2·543 \times 10^{-3}$	$2·533 \times 10^{-3}$	3·910

the rising connecting tube, and sinks to the bottom of the side limb of the apparatus. The influence of diffusion was shown to be negligible in the course of the experiments, for identical results were obtained in similar experiments of long and short duration, in which the effects of diffusion would differ.

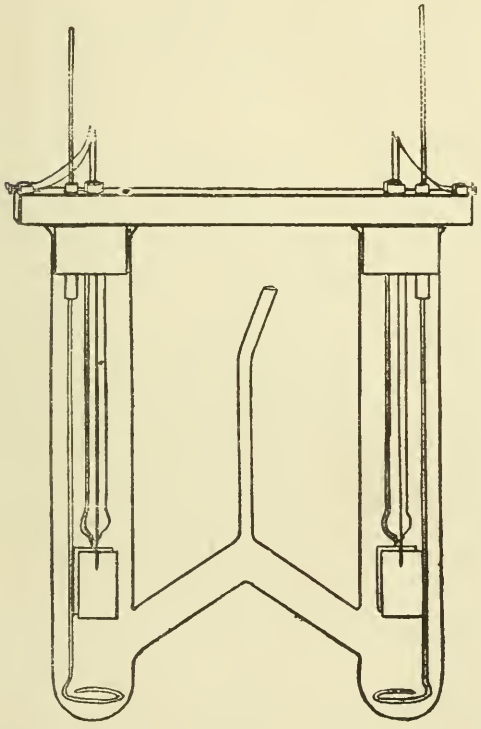


FIG. 1.

The mode of procedure is as follows :—A solution of pure potassium chloride is made up of a convenient strength by weighing out the salt. This solution is diluted by adding a known weight of water. The resistance of the solution so prepared, when placed in the cell, is measured between each pair of electrodes. From the specific resistance of potassium chloride solutions, as given by Kohlrausch, this gives the cell constant of each end of the apparatus, treating each vertical limb as a separate resistance cell. After careful washing, the apparatus is then filled with a solution of sulphuric acid, the concentration of which is known to be approximately that required. By measuring the resistance between each pair of electrodes, two values for the exact concentration may then be calculated from Kohlrausch's tables.

The apparatus is now ready for a migration experiment. A current from a battery of 50 or 100 small storage cells is passed through the apparatus from one pair of electrodes to the other, each pair in this part of the work being used as a single electrode. The strength of the current is determined by passing it through a standardised shunted galvanometer, and thus the total amount of chemical decomposition calculated from the known values of the electro-chemical equivalents. After a definite time has elapsed, the circuit is broken, the two parts of the solution are separated by increasing the pressure of the air in the inverted V tube, and measurements are taken of the resistance between each pair of electrodes as before. The change in concentration in the solution round each electrode may thus be estimated, and, by extracting and weighing each part of the solution, the total change in contents of acid calculated.

In a solution of sulphuric acid, the ions are hydrogen and the sulphion group SO_4. Hydrogen is liberated as such at the cathode, but the sulphion reacts with the water to form sulphuric acid and oxygen, the latter escaping. Thus when 1 grm.-equivalent of hydrogen is evolved, 1 grm.-equivalent of acid is re-formed at the anode by the secondary action of the sulphion and the water. But, besides this change, that due to migration must be considered. If the cation of any salt solution drifts one way with a velocity u, and the anion the other with a velocity v, the amount of separation in unit time is $u+v$. In accordance with the principle of migration, there is a loss of salt measured by v at the cathode, and a loss measured by u at the anode. But in our case there is also a gain of $u+v$, equal to the total amount of decomposition, at the anode. Thus the resultant gain at the anode is $u+v-u$ or v, and the resultant loss at the cathode is also v. Hence, by determining the loss and gain, we get two independent values for the same quantity, and the concordance between them gives a preliminary test of the success of the apparatus and method.

Finally, a knowledge of the value of the current and its time of flow gives $u+v$, and enables us to calculate $v/(u+v)$, the transport ratio.

After some changes, the apparatus in its final form gave satisfactory results as tested by the agreement between the loss of acid at the cathode and the gain at the anode. Details of one experiment may be given as an example.

Resistance before passage of current .. { Anode vessel—7102, 7106, 7112 = 7107 mean in ohms. Cathode vessel—6252, 6258, 6264 = 6258 mean in ohms.

Current from 50 cells (= 100 volts) passed for fifteen minutes—

Resistances. . { Anode vessel .. 8316, 8263, 8296 = 8297 Cathode vessel . 5452, 5461, 5464 = 5462

Weight of solutions in anode vessel .. = 53·25 grms.
Weight of solutions in cathode vessel . = 57·00 „

From these results it follows that the conductivity of the solution before the passage of the current was $1·408 \times 10^{-5}$.

After the passage of the current the conductivity of the anode solution was $1·614 \times 10^{-5}$, and of the cathode solution $1·219 \times 10^{-5}$.

The concentration of the original solution was $4·042 \times 10^{-5}$ grm.-equivalent per 1000 grms. From the known curve between concentration and equivalent conductivity, the concentration of the final anode and cathode solutions was estimated as $4·575 \times 10^{-5}$ and $3·546 \times 10^{-5}$ respectively. Then, from the observed total masses of their solutions, the total gain and loss in contents was calculated as

$2{\cdot}843 \times 10^{-7}$ grm.-equivalent and $2{\cdot}831 \times 10^{-7}$ grm.-equivalent respectively.

A rough estimate of the current gave $1{\cdot}491 \times 10^{-4}$ ampère, and, as the total number of grm.-equivalents liberated, $1{\cdot}390 \times 10^{-6}$. Thus the transport ratio is approximately $0{\cdot}2836/1{\cdot}390 = 0{\cdot}205$.

No stress can be laid on this last result, as the method of measuring the current was not finally adopted as satisfactory, but the concordance between the gain of acid at the anode and the loss at the cathode showed that, so far, the method was successful.

At this point the pressure of other duties prevented the writer from continuing the experiments, but, by the aid of the Government Grant Committee of the Royal Society, the services of Mr. H. H. Paine were secured. The work described in Part II. of this paper is Mr. Paine's; the present writer only exercised a general supervision over the course of the research.

(To be continued).

SOME EFFECTS OF SUNLIGHT UPON COLOURLESS GLASS.

By ROSS AIKEN GORTNER.

WITHIN recent years a number of instances have been reported from various parts of the world concerning the violet coloration of glass when exposed to the sunlight (Crookes, CHEMICAL NEWS, 1905, xci., 73; Avery, *Journ. Am. Chem. Soc.*, 1905, xxvii., 909; Simpson, CHEMICAL NEWS, 1905, xci., 236; Rueger, *Journ. Am. Chem. Soc.*, 1905, xxvii., 1206; Alway and Gortner, *Am. Chem. Journ.*, 1907, xxxvii., 1).

Fischer (*Ber.*, 1905, xxxviii., 946) has induced the same change in colourless glass, containing a comparatively small proportion of manganese, by exposure to the rays of a mercury lamp, thus showing that the change is due to the ultraviolet rays.

Up to the present time only one instance, which was observed by the writer (*Am. Chem. Journ.*, 1907, xxxvii., 1), has been reported indicating the time of exposure actually required to produce the change in the colour of the glass.

On July 9, 1906, twenty-two specimens of glass were firmly fastened to a board by means of aluminium wire, and the board exposed upon the slate roof of a building at Lincoln in a position facing the south and inclined at an angle of about 45°. The spot selected was about 75 feet above the ground and was exposed to the direct rays of the sun for the entire day excepting, perhaps, in June and July for an hour before sunset, when a low tower on the west cast a shadow on the board. The specimens, when on the building, were at an elevation of about 1200 feet above sea level.

Specimens 1 to 12 inclusive were rectangular four-ounce bottles of the same make, and were obtained from a local dealer. They were exposed, filled with various substances, Nos. 1 to 6 being filled with chalk coloured, respectively, with picric acid, indigo, methyl violet, "wasserblau," malachite green, and sodium eosin. No. 7 was filled with manganese dioxide, No. 8 with lampblack, No. 9 with sodium eosin solution, No. 10 with potassium permanganate crystals, No. 11 with chalk, while No. 12 was exposed empty. Nos. 7, 8, and 10 were filled with their respective contents in order to determine what truth there might be in the theory of Chas. Rueger that glass might become "violet by lying for some time in the proximity of bodies heavily charged with manganese" (*Journ. Am. Chem. Soc.*, 1905, xxvii., 1206). No. 13 was a bottle of a different make and was exposed filled with potassium chromate crystals. No. 14 was the base of a broken goblet which was found upon the street, and which as yet showed no trace of violet coloration, although it might have been exposed to the sunlight for some time. No. 15 was a small glass funnel, No. 16 a small round solution bottle, No. 17 a 50 cc. Erlenmeyer flask of Jena glass, No. 18 an ordinary round 50 cc. flask, No. 19 a small homœopathic vial of American manufacture, No. 20 a piece of hard glass tubing, and Nos. 21 and 22 pieces of soft glass tubing. Nos. 15, 16, 17, 20, 21, and 22 were secured from the "Vereinigte Fabriken," Berlin.

One month after exposure the specimens were examined and it was found that Nos. 13, 14, 21, and 22 had become slightly violet, No. 13 being of so decided a violet tinge that the coloration was noticeable several feet away.

The specimens of glass then remained undisturbed until the 21st of March, 1907, when they were again examined. At that time they all showed some violet coloration excepting Nos. 15, 16, 17, and 20, which still remained colourless. Nos. 13 and 21 had by this time become intensely violet. No. 22 could not be found, evidently having been blown away by the wind.

On May 31, 1907, the board was removed from the roof, and the bottles, after being cleaned, were given a close inspection, with the following result:—No. 1 was distinctly violet on the upper face, less violet on the sides, but still enough so that the coloration was plainly visible, and almost colourless on the back. Nos. 2, 4, 5, 6, and 11 differed in no way from No. 1. No. 3, which had contained chalk coloured with methyl violet, was of a deeper colour on the upper face and sides and was also of a faint violet on the back. No. 7 (filled with manganese dioxide) and No. 8 (filled with lampblack) were indistinguishable from each other, being less violet on the surface and sides than the preceding numbers and showing almost no colour on the back. No. 9 had been broken by the freezing of its contents; the violet tinge on the face and sides was pronounced, and on the back less so. No. 10, containing potassium permanganate crystals, was the least coloured of the series 1—12, being slightly less violet than Nos. 7 and 8. There was a faint violet tinge upon the upper face and almost no colour whatever upon the sides and back. No. 12, being empty, was of a uniform violet throughout, and the colour could not be distinguished from that of the face of No. 1. No. 13 was a very intense violet upon the face and sides and of a deep violet on the back. This is the best specimen of violet-coloured glass that I have been able to secure in Nebraska, although it is surpassed in intensity of coloration by some specimens from the steppes of Canada and from New Mexico. (The specimens from New Mexico were secured from Dr. Avery). No. 14 was of a deep violet throughout, being more intense in colour than No. 12 and much less intense than No. 13. The shade was slightly deeper than on the back of No. 13. Nos. 15, 16, 17, and 20 showed no trace of violet coloration. Nos. 15, 16, and 20, as will be shown later in the table of analyses, contained no manganese, and No. 17, although containing manganese, was not coloured violet by the action of the sunlight. An explanation for this may be found in the composition of Jena glass which may prevent the necessary chemical change from taking place. Fischer met with similar results when Jena glass was exposed to the rays from a mercury lamp (*Ber.*, 1905, xxxviii., 946). Nos. 18 and 19 were distinctly violet throughout. No. 21 was distinctly violet when seen from the side, even at a distance of several feet, and when viewed lengthwise the violet coloration was very intense, being but a shade lighter than No. 13.

In order to obtain the manganese content, the method of H. Noll was employed (*Centralbl.*, April 17, 1907, i., 1223). Portions of the specimens were ground to a powder, fused with sodium and potassium carbonates, dissolved in dilute hydrochloric acid, precipitated with ammonia and bromine water, and allowed to stand for twelve hours. The precipitate was then filtered out, washed, and treated with 1 grm. potassium iodide and 4 cc. concentrated hydrochloric acid. After standing for five minutes the iodine set free was titrated with N/100 sodium thiosulphate. From the iodine set free the manganese is calculated.

No. of sample.	Description of sample.	Per cent of manganese.	Colour after one month.	Colour after eight months.	Colour after eleven months.
15.	Small funnel (Verein. Fabrik.)	0·000	None.	None.	None.
16.	100 cc. bottle (Verein. Fabrik)	0·000	None.	None.	None.
20.	Hard glass tubing (Verein. Fabrik.)	0·000	None.	None.	None.
14.	Base of goblet	0·049	Slight.	Distinct.	Deep.
17.	50 cc. Erlenmeyer flask (Jena glass)	0·072	None.	None.	None.
1.	Bottle with chalk coloured with picric acid	0·075 to 0·087	None.	Light.	Distinct.
2.	Do. do. indigo			Light.	Distinct.
3.	Do. do. methyl violet			Distinct.	Deeper than No. 1.
4.	Do. do. "wasserblau"			Light.	Distinct.
5.	Do. do. malachite green			Light.	Distinct.
6.	Do. do. sodium eosin			Light.	Distinct.
7.	Bottle with manganese dioxide			Pale.	Light.
8.	Bottle with lamp-black			Pale.	Light
9.	Bottle with sodium eosin solution			Distinct (broken).	Distinct.
10.	Bottle with potassium permanganate crystals			Faint.	Very light.
11.	Bottle with chalk			Distinct.	Distinct.
12.	Bottle, empty			Distinct.	Distinct.
19.	Homœopathic vial (American manufacture)	0·14	None.	Distinct.	Deep.
18.	Round flask (American 50 cc.)	0·17	None.	Distinct.	Deep.
21.	Soft glass tubing	0·20	Pale.	Distinct.	Deep.
13.	Bottle with potassium chromate crystals	0·34	Distinct.	Deep.	Very deep.
22.	Soft glass tubing	(?)	Distinct.	Lost.	Lost.

The colour of the beads which were obtained by the fusion ranged from a deep purple in No. 13 to colourless in Nos. 15, 16, and 20. The range of coloration was in the following order:—13, 11, 19, 18, 21, 14, and 17, 13 being the most coloured and 17 the least. The beads obtained from Nos. 1 to 12 were indistinguishable, and therefore No. 11 was selected to represent the series.

The accompanying table gives the percentage of manganese and shows the relation of this to the change in colour on the face of the specimen. "Slight" means slightly violet, "pale" means pale violet, &c.

The influence of the exposure of glass is well illustrated by the colour of the basement windows of a church near Lincoln which has been built for five years. The windows are of pressed glass, and on the south and west sides are of such a distinctly violet colour as to be easily noticeable a hundred yards away, while on the north and east sides there is almost no coloration. When closely examined, the violet coloration is so intense as to be comparable only to the deeper coloured glass found on the high plains of Canada. The coloration is as deep as that of No. 13 although the manganese content is only 0·126 per cent, the deep colour being probably due to the length of exposure.

Beside the specimens of violet-coloured glass secured in this vicinity, the writer has found many scattered over eastern and northern Nebraska, and has received some from the second steppe of Canada. The latter came from southern Saskatchewan at an elevation of about 2000 feet.

Summary.

Glass containing a relatively large percentage of manganese may show a violet coloration when exposed to sunlight for a period of less than a month, the degree of coloration being proportional to the manganese content.

Exposure of less than a year will produce a violet coloration in most glasses containing only a small percentage of manganese, but this coloration will become more pronounced when the time of exposure is increased.

Should a glass be coloured violet by the action of sunlight, proof is furnished that the glass contains manganese. However, not all glasses containing manganese are coloured violet by exposure to sunlight, as is shown by the Jena Erlenmeyer.

A background or subsoil containing manganese or ores of manganese will have no influence upon the coloration of glass lying upon it.

A violet background is more favourable to the action of the ultraviolet rays than other colours: white, yellow, blue, and red act alike and seem to have no effect, while brown and black seem to have a retarding effect.—*American Chemical Journal*, 1908, xxxix., p. 157.

THE ESTIMATION OF CHROMIUM AS SILVER CHROMATE.

By F. A. GOOCH and L. H. WEED.

It has been shown by Autenrieth (*Ber.*, xxxv., 2057) that when chromic acid is added to a boiling solution of silver nitrate, or when a soluble chromate or dichromate is added to a solution of silver nitrate previously acidified with nitric acid, or when silver chromate is treated with nitric acid, silver dichromate is formed; and that, on the other hand, it is silver chromate which is precipitated when silver nitrate in excess is added to a solution of a soluble dichromate, cold or hot, the reaction proceeding according to the equation —

$$4AgNO_3 + K_2Cr_2O_7 + H_2O = 2Ag_2CrO_4 + 2KNO_3 + 2HNO_3.$$

The characteristics of both silver dichromate and silver chromate have recently been summarised and further studied by Margosches (*Zeit. Anorg. Chem.*, xli., 68; l., 231), but so far as we know there is in the literature no account of procedure for the exact quantitative determination of either chromium or silver based upon the characteristics of either of these salts. The solubility of silver dichromate in water and in ordinary solutions is such as to preclude the use of this substance as the final product of a quantitative process depending upon precipitation. The solubility of silver chromate in a moderately large volume of water is not inconsiderable, and the solvent action of free acid, even acetic acid in quantity, is marked. We have found, however, that the precipitation of silver chromate is practically complete in a solution only faintly acid with acetic acid and in presence of a large excess of silver nitrate. If such a precipitate is collected in the filtering crucible and washed with a dilute solution of silver nitrate, until no other impurities remain, silver chromate does not dissolve, and the excess of silver nitrate may be removed by the cautious use of water without appreciable effect upon the precipitate. The present paper has to do with the determination of chromium as silver chromate.

In the experiments of which the details are given in the table, the general treatment just described was put to the practical test. Given amounts of potassium dichromate were weighed out and dissolved in hot water, as in

Experiments 11 and 12, or given amounts of a solution of potassium dichromate of known strength were run from a burette into a beaker and heated to boiling, as in Experiments 1 to 10. To the hot solution of the dichromate was added, drop by drop, a solution of silver nitrate in considerable excess, and the mixture was again brought to the boiling-point. Ammonium hydroxide was added until the clear liquid became colourless and turned litmus-paper blue; then acetic acid was added cautiously until the reaction of the solution was distinctly acidic to litmus. After standing for at least half-an-hour the precipitate was filtered off on asbestos in a perforated crucible, washed first with a dilute solution of silver nitrate and then with 20 cc. to 30 cc. of distilled water applied in small portions, and dried with gentle heating to a constant weight. In Experiments 1 to 10 the drying was done in an air-bath heated to 135°; in Experiments 11 and 12 the crucible and precipitate were heated gently over the free flame. In Experiments 7 and 8 the precipitation was made in presence of 5 grms. of ammonium nitrate, and in 9 and 10 in presence of 5 grms. of sodium nitrate, to test the effect of each of these substances upon the process. In no case did the filtrate, with the washings, show by the lead acetate test the presence of a chromate.

The Precipitation of Silver Chromate.

	$K_2Cr_2O_7$ taken.	$AgNO_3$ used in precipitation.	Volume at precipitation.	Ag_2CrO_4. Found.	Theory.	Error.
	Grm.	Grm.	Cc.			
1.	0·0921	0·4248	100	0·2072	0·2076	−0·0004
2.	0·0921	0·4248	100	0·2073	0·2076	−0·0003
3.	0·0921	0·4248	100	0·2075	0·2076	−0·0001
4.	0·0921	0·4248	100	0·2074	0·2076	−0·0002
5.	0·0921	0·4248	100	0·2075	0·2076	−0·0001
6.	0·0921	0·4248	100	0·2073	0·2076	−0·0003
7.	0·0921	0·4248	100	0·2073	0·2076	−0·0003*
8.	0·0921	0·4248	100	0·2075	0·2076	−0·0001*
9.	0·0921	0·4248	100	0·2080	0·2076	+0·0004†
10.	0·0921	0·4248	100	0·2070	0·2076	−0·0006†
11.	0·5801	3·0000	150	1·3087	1·3082	+0·0005
12.	0·7352	3·0000	200	1·6573	1·6574	−0·0001‡

* The precipitation was made in presence of 5 grms. of NH_4NO_3.
† The precipitation was made in presence of 5 grms. of $NaNO_3$.
‡ An excess of 1 cc. of 40 per cent acetic acid was added before filtering.

From the results of these experiments it is apparent that accurate determinations of chromium taken as the chromate or dichromate may be secured by precipitating silver chromate in presence of an excess of silver nitrate, making the solution ammoniacal and then faintly acid with acetic acid, transferring the precipitate to the filtering crucible, washing with a dilute solution of silver nitrate, and, after other soluble impurities have been removed, finishing the washing with small amounts of water applied in successive portions.—*American Journal of Science*, xxvi., p. 85.

NOTES ON A NEW PRIMARY VOLTAIC CELL OF THE DANIELL TYPE.

By JAMES STRACHAN.

THE voltaic cell about to be described was devised by the writer about eight years ago, and was set up for the first time in the chemical laboratory of George Heriot's Hospital. While experimenting with various chlorinated compounds, such as oxychlorides, perchlorides, and tetrachlorides, with regard to their suitability as depolarisers in primary voltaic cells, tetrachloride of lead ($PbCl_4$) was found to be a powerful and efficient depolariser. Since that time I have proved on various occasions the usefulness of this cell in the laboratory, and apart from its practical value, it is also of great theoretical interest as an illustration of electro-chemical depolarisation.

Name of cell.	Anode.	Excitant.	Cathode.	Depolariser.	E.M.F. (volts).	Advantages.	Disadvantages.
De la Rue	Zinc	NaCl or $ZnCl_2$	Silver	AgCl	1·3—1·4	Compactness.	Expense.
Von Helmholtz . .	Zinc	$ZnCl_2$	Mercury	Hg_2Cl_2	1·0	Constant action.	Expense.
Becquerel (modified)	Zinc	HCl	Lead	$PbCl_2$	0·5	Cheapness.	Easily polarised.
Papst	Iron or tin	Fe_2Cl_6 or $SnCl_4$	Carbon	Fe_2Cl_6 or $SnCl_4$	0·4—0·7	Simplicity and constant action.	Low E.M.F.
Maron	Zinc	H_2SO_4	Carbon	Fe_2Cl_6	1·5	Recuperates when exhausted.	High resistance.
Gerardin	Iron	Water	Carbon	Fe_2Cl_6+HCl+HNO_3	1·0	Cheapness.	High resistance chlorine evolved.
Niaudet	Zinc	NaCl	Carbon	CaCl(OCl)	1·5	Cheapness.	High resistance, and evolves fumes of chlorine.
Fitch	Zinc	NH_4Cl	Carbon	$NaClO_3$+$KClO_3$	1·1	Simplicity.	Easily polarised.
Heriot, No. 1. . .	Zinc	NH_4Cl+$ZnCl_2$+HCl	Carbon	$PbCl_4$ in HCl	1·5	Constant action and low resistance.	Odour of chlorine.
Heriot, No. 2. . .	Iron	NH_4Cl+$ZnCl_2$+Fe_2Cl_6	Carbon	$PbCl_4$ in HCl	0·95	Cheapness.	Odour of chlorine.

The new cell is of the Daniell type, and in it the copper element is replaced by carbon, the copper sulphate by tetrachloride of lead, and the dilute sulphuric acid, surrounding the amalgamated zinc, by dilute hydrochloric acid, or other excitant.

The action of nascent hydrogen upon the tetrachloride of lead is similar to that which takes place upon the copper sulphate in a Daniell cell, metallic lead being deposited in place of copper, and hydrochloric acid formed in place of sulphuric acid, as in the following equations:—

$$\text{Daniell cell: } H_2 + CuSO_4 = Cu + H_2SO_4.$$
$$\text{Heriot cell: } 2H_2 + PbCl_4 = Pb + 4HCl.$$

The cell may be conveniently arranged as in the accompanying sketch. Within an outer stoneware jar, O, are placed a number of carbon rods, C C, which are connected electrically by the heavy leaden cover, L, to form the negative element. The rods may consist of stout arc-light carbons, the ends of which are coppered by electro-deposition previous to casting the leaden cover around same. In the centre of the cover is a circular aperture which admits neatly the insertion of the porous earthenware pot, P, within which stands the positive element, an amalgamated zinc cylinder, Z. An acid solution of lead tetrachloride surrounds the carbon rods, and the zinc is immersed in a suitable excitant, which may consist of dilute hydrochloric acid (1 in 7 of water), zinc chloride (5 to 10 per cent solution), or ammonium chloride (15 to 20 per cent solution). Mixtures of these excitants may be employed, and the following gives good results:—

Ammonium chloride	100 grms.
Zinc chloride	10 „
Hydrochloric acid	20 cc.
Water to 1 litre.	

Unfortunately, lead tetrachloride is not an article of commerce, and the preparation of the depolariser presented at first some difficulties. The usual methods of preparing $PbCl_4$ solution in the laboratory are:—

1. Passing chlorine gas into hydrochloric acid containing freshly precipitated lead dichloride in suspension: $PbCl_2 + Cl_2 = PbCl_4$.
2. Dissolving lead peroxide in cold concentrated hydrochloric acid: $PbO_2 + 4HCl = PbCl_4 + 2H_2O$.

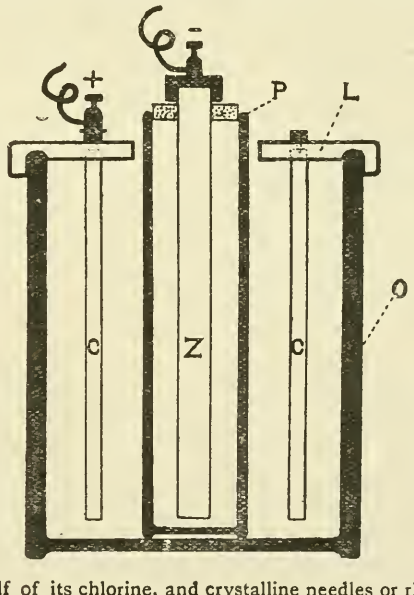
The latter method is the simpler, but it is both dangerous and disagreeable to perform, as the action is incomplete, $PbCl_2$ being precipitated with the evolution of much chlorine. After some experimenting it was found that freshly precipitated lead peroxide dissolves quite readily in cold strong hydrochloric acid. The precipitate of PbO_2 may be best prepared by dissolving 100 grms. of lead acetate in 500 cc. of cold water, and then adding a strong solution of calcium hypochlorite, prepared by lixiviating 110 grms. of fresh bleaching-powder in 1 litre of water, and decanting. Yellow PbO is at first precipitated, but after a few hours it becomes completely oxidised to the puce-brown peroxide. The heavy PbO_2 sinks to the bottom, and the bulk of the supernatant liquor may be poured away. The remaining pasty mass of peroxide is then stirred up to a creamy consistency and added gradually to about 500 cc. of cold concentrated hydrochloric acid in a Winchester quart bottle. The latter is kept cold by immersion in running water, and is gently shaken after each addition of the peroxide. The PbO_2 dissolves readily with evolution of a small amount of chlorine, forming an acid liquor of a bright orange-yellow colour, which is the depolariser as used in the cell.

A much simpler method of preparing the solution of tetrachloride suggested itself, and was found to work well in practice. 100 grms. of lead acetate were dissolved in 300 cc. of cold water, and 110 grms. of fresh bleaching-powder mixed with same in a strong pressure bottle. The mixture rapidly became brown in colour, due to the formation of lead peroxide. When quite cold about 700 cc. of strong commercial hydrochloric acid were added, and the pressure bottle rapidly sealed. During the ensuing action the bottle was cooled in running water. The brown mixture dissolved rapidly to form a solution of calcium chloride and lead tetrachloride, which was used as the depolarising fluid. This operation is rather a dangerous one to perform, and care must be taken to guard against the sudden evolution of the poisonous chlorine. When a glass pressure bottle is employed, the mixture of lead acetate and bleaching-powder should be made in a mortar with enough water to form a creamy paste, and the latter added gradually to the hydrochloric acid contained in the bottle, sealing and agitating after each addition. Large quantities of lead tetrachloride could be made very easily by this method by dissolving the lead acetate and chlorinated lime in lead-lined cylinders of wrought iron.

The acid solution of lead tetrachloride should not be exposed to sunlight, as it is then decomposed, oxygen being evolved and crystalline plates of $PbCl_2$ precipitated:—

$$PbCl_4 + H_2O = PbCl_2 + 2HCl + O.$$

The solution is also decomposed very readily by many organic substances, since it possesses the oxidising properties of chlorine water in an intensified degree. In the presence of oxidisable organic matter, $PbCl_4$ yields



one-half of its chlorine, and crystalline needles or rhombs of $PbCl_2$ are precipitated. As a depolariser it is rapid, efficient, and constant in its action. On a closed circuit this cell cannot be polarised while any of the $PbCl_4$ remains in the solution around the negative element. In these respects it resembles the Daniell cell, but possesses a higher electro-motive force and a much lower resistance. Lead tetrachloride has a rather serious disadvantage, however, in the powerful odour of chlorine that attends its preparation and use. The cell must be charged either in the open air or in a draught chamber. While in use, the escape of chlorine fumes is entirely prevented by the closely-fitting leaden cover of the cell, the space between the porous pot and the inner edge of the cover being sealed, for the time being, with soft paraffin-wax. After the cell has been in action for some time the carbon rods become coated with a spongy deposit of metallic lead, which is easily removed by scraping with a spatula. Through continued action the pores of the carbon rods sometimes become filled up with coherent metallic lead. This may be removed by dipping the carbons into strong nitric acid. When the cell is required to give as large an output of current as possible, the excitant should be strengthened by the addition of hydrochloric acid (1 part to 4 parts of water), the zinc

should be heavy and well amalgamated, and the carbon rods should be replaced by several carbon plates surrounded by tightly-packed granules of the same material. With the exception of silver chloride, lead tetrachloride is the most efficient depolariser, using chlorine in union with a metallic base.

The accompanying table shows in comparison various cells, using such depolarisers and their relative values.

As shown in the table, iron may be employed in the new cell in place of zinc, when the E.M.F. drops from 1·5 to 0·95. When iron is used as the positive element, the hydrochloric acid should be left out of the excitant, and the latter be mixed as follows:—

Ammonium chloride	100 grms.
Zinc chloride	10 „
Ferric chloride	10 „

Water to 1 litre.

There is much more local action with iron than with zinc, and this action appears to be much less when tinned iron is employed.

I am much indebted to Mr. James D. Fulton, M.A., B.Sc., of Edinburgh, for the following results of experiments determining the E.M.F. of this cell, using zinc and iron as the positive elements with various excitants; and carbon as the negative element immersed in the acid solution of $PbCl_4$:—

Excitant used.	Electromotive force (volts).	
	With zinc.	With iron.
Hydrochloric acid, dilute	1·41	0·83
Zinc chloride solution	1·22	0·73
Ammonium chloride solution ..	1·51	0·95

The above figures were obtained by comparison with a standard Daniell cell, E.M.F. 1·111, and were further checked with a single cell of an accumulator in place of the standard, consistent results being obtained.

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THE EXISTENCE OF PLATINUM METALS IN CHEMICALS USED FOR ASSAYING.*

By JOHN G. ROSE, Government Analyst, Cape Town.

During the past twelve months upwards of fifty samples of rock have been assayed in the Government Analytical Laboratory, Cape Town, for platinum, in all but two cases with negative results. These two exceptions having yielded such minute traces it was a matter for considerable surprise when a sample of acid dolerite from Stutterheim in the Eastern Province, and a sample of white quartz from Swellendam, in the Western Province, assayed at the same time, *i.e.*, some four weeks ago, were each found to contain 4·8 grains of platinum per ton of 2000 lbs.

The possibility of the platinum having come from the rocks appeared to be so remote that it was deemed advisable to test the assay materials in order to ascertain whether they were platiniferous. The hydric sodic carbonate having been proved free from platinum on previous occasions, only the litharge and the borax were examined. In place of possibly platiniferous rocks four assay ton charges of sea-sand were used, and it was then found that when 160 grms. of the litharge previously used were made into a charge with platinum-free borax, a nil result as regards platinum followed, whereas, when 40 grms. of the borax employed in the above assays was coupled with platinum-free litharge, 0·04 of a mgrm. of platinum was invariably obtained as the result of the assay.

In such cases the silver bead from the assay showed the peculiar dull spongy appearance which is characteristic of beads containing over 5 per cent platinum. On dissolving this particular bead in hot concentrated sulphuric acid a few specks of a black powder were left which weighed 0·04 of a mgrm. This powder when dissolved in aqua regia, the solution being evaporated to dryness and the residue taken up with water, gave the platinum reaction with potassium iodide. Lest it should be thought that the platinum could have been derived from the sea-sand an assay was made containing only borax, platinum-free litharge, and sufficient carbon to produce a lead button. In this case, too, the bead produced contained the quantity of platinum already stated.

In order to confirm this result further assays were undertaken, one on 200 grms. of borax and another on 1000 grms. of borax, with the following results:—

200 grms. of borax yielded 0·26 mgrm. of black powder,
1000 grms. of borax yielded 1·42 mgrms. of black powder.

The 0·26 of a mgrm., when converted into chloride and treated with ammonia chloride and alcohol, yielded the characteristic yellow precipitate, which, upon ignition, was converted into spongy platinum, and from this was once more obtained yellow ammonic chloro-platinate.

The 1·42 mgrms., when treated with aqua regia, did not completely dissolve, but left a residue weighing 0·12 of a mgrm. This residue did not appreciably lose weight after eight hours' treatment with boiling aqua regia, and appeared under the lens as greyish metallic spangles, which were unaltered by ignition. Unfortunately there was not sufficient borax available from which to obtain enough of this substance to determine its nature. Having regard, however, to the foregoing tests and the manner in which the residue was obtained, it seems highly probable that it consists of iridium osmide.

The chloride soluble in water was converted into ammonic chloro-platinate.

The results available, therefore, are as follows:—

40 grms. borax used for assaying dolerite gave 0·04 mgrm. platinum.
40 grms. borax used for assaying quartz gave 0·4 mgrm. platinum.
40 grms. borax used with sea-sand in place of rock gave 0·04 mgrm. platinum.
200 grms. borax used with sea-sand in place of rock gave 0·26 mgrm. platinum.
1000 grms. borax used with sea-sand in place of rock gave 1·30 mgrms. platinum and 0·12 mgrm. osmiridium.

It therefore appears certain that the borax contains platinum to the amount of 1·3 parts per million, *i.e.*, 0·00013 per cent.

In casting about for the source of platinum it seemed possible that this impurity might have been introduced by fusing the borax in platinum vessels, assuming such to have been used in its manufacture. In order to test this theory 250 grms. of platinum-free borax was fused in a platinum basin at a red heat for four hours. The melt was allowed to cool, and when removed from the dish 200 grms. of it yielded 0·6 mgrm. platinum. A second 250 grms. was treated in a similar manner, but in this case so as to obviate the possibility of any platinum having been mechanically removed by the hand-fused borax, the latter was poured while still liquid into clean sand. 200 grms. of this yielded 0·46 mgrm. platinum. A third quantity confirmed the result obtained in the second experiment.

It is thus shown that fused borax has a very distinct action on platinum basins.

It may be interesting to note that up to the time that platinum was discovered in the borax ordinary assay borax had been employed. The comparatively large quantities of platinum were found in Merck's "m. g. r. puriss. borax." Even ordinary assay borax is not always entirely free from platinum, traces of the noble metal having recently been found to exist in a sample at present in use in the Government Laboratory.

Under ordinary circumstances the occurrence of such minute traces of platinum in an assay chemical would not

* Read before the Cape Chemical Society, Cape Town, July 17, 1908.

be of more than academic interest, for it would probably not be seriously asserted that rocks containing the infinitesimal traces of the metal which the use of this platiniferous borax would make them appear to contain could pay for working, and as a rule, therefore, time was not wasted in looking for such traces. In view, however, of recent allegations regarding the occurrence of platinum metals in South African rock formations the matter assumes a somewhat different complexion.

The assay balance used in the foregoing experiments turns easily with one-fiftieth mgrm., and with care can be made to indicate one-hundredth mgrm.

TECHNICAL METHOD FOR THE DETERMINATION OF LEAD IN ORES, &c.

By A. H. LOW.

THE following scheme is the result of many attempts on my part to improve the methods wherein lead is separated as oxalate and subsequently titrated with permanganate. I have used the method as described below for several months, and have found it more satisfactory for technical work than any other with which I am acquainted. Duplicate assays usually check within one-tenth of 1 per cent. A test of five portions of pure lead, weighed so as to approximately represent 3, 12, 20, 45, and 60 per cent of lead in an ore, and put through the entire process, showed errors of −0·01, −0·06, +0·01, +0·05, and +0·05 per cent respectively, the average error being 0·036 per cent. The permanganate was standardised on about 0·200 grm. of lead.

Chromate-Oxalate Method.—Take 0·5 grm. of ore and treat in a 6-oz. flask by the usual methods to obtain the washed lead sulphate, &c., on a 9 cm. filter. Dissolve the lead sulphate on the filter by stirring it up repeatedly with a jet of hot sodium acetate solution contained in a wash-bottle, receiving the filtrate in the original flask. Prepare the solvent by diluting a cold saturated solution of commercial sodium acetate with an equal bulk of water and adding 40 cc. of 80 per cent glacial acetic acid per litre. To test if the extraction of the lead sulphate is complete, the flask may be replaced by a small beaker, the washing continued, and a little potassium dichromate added to the filtrate. If any lead chromate is produced, the mixture may be added to the clear solution in the flask. Agitate the extract in the flask and heat it if necessary to re-dissolve any separated precipitate. Add 10 cc. of a 5 per cent solution of commercial potassium dichromate, heat to boiling, and boil gently for a few minutes to render the precipitate basic and easily filtered. The change is shown by its becoming reddish yellow in colour. Filter hot, wash out the flask with hot water, and then wash the precipitate only once, simply to clean the upper edge of the filter. Place a wide-necked funnel in the flask, open the filter and spread it against the wall of the funnel, and wash off the lead chromate with a jet of hot oxalic acid solution, using from 25 to 40 cc. Rinse down any adhering chromate in the flask with hot water. The oxalic acid solution consists of a cold saturated solution of commercial acid 1 part, water 3 parts. Heat nearly to boiling in a wash-bottle. To the mixture in the flask add grain alcohol and then boil until the chromic acid is all reduced and the lead converted to oxalate. Remove from the heat, add 30 cc. of cold water and cool thoroughly, best under the tap or in cold water. When cold, filter through an 11 cm. filter, wash out the flask thoroughly with cold water, and then wash filter and precipitate ten times with cold water. Place 5 cc. of strong sulphuric acid in the flask, dilute first with a little cold water and then with hot water to about 125 cc. Add the filter and precipitate and titrate to the usual pink tinge with standard potassium permanganate solution. The solution used for iron will serve, although too strong for the best work. Theoretically, the oxalic acid ($C_2O_4H_2.2H_2O$) value of the permanganate multiplied by 1·642 will give the lead value, but owing to slight losses as sulphate, oxalate, &c., and the fact that the lead oxalate is not perfectly pure, the factor 1·669 will give a closer approximation. On this basis, for 0·5 grm. of ore taken for assay, the solution should contain 1·5185 grms. of potassium permanganate per litre, in order that 1 cc. may equal 1 per cent lead. It is best to standardise on about 0·200 grm. of pure lead dissolved in a little 1 : 2 nitric acid and put through the entire process.

Notes.

The lead oxalate formed in the above process is not pure white, but yellowish, and still contains about 1 per cent of lead chromate. It appears to be sufficiently uniform in its nature to give accurate results.

Instead of dropping filter and precipitate into the flask for titration, as described above, a neater method of procedure is as follows:—Place the flask under the funnel and pour through and over the filter about 75 cc. of hot dilute acid, containing 5 cc. of strong sulphuric acid, and then wash the filter and residue well with hot water, so that the final bulk of the filtrate will be about 125 cc. Titrate the hot liquid as before. This method takes a little longer and gives practically the same results as the simpler way, but it has the advantage of a permanent end-point, there being no organic matter present to slowly decolorise the pink tinge.

Calcium does not interfere with the method, nor does antimony. Bismuth in small amounts is without material influence. Ten per cent of bismuth added to a mixture containing about 23 per cent of lead raised the result 0·36 per cent, most of the bismuth being removed as sulphate and chromate.—*Journal of the American Chemical Society*, xxx., p. 587.

A SEPARATION OF IRON FROM MANGANESE.

By RICHARD B. MOORE and IVY MILLER.

IF to a solution of ferric chloride containing free hydrochloric acid, pyridine, in slight excess, be added, the iron is completely precipitated as hydroxide. Aluminium, chromium, and zinc, under such conditions, are not completely precipitated, while manganese, nickel, and cobalt remain in solution. This method can therefore be used to separate iron from the last three metals. The present paper deals only with the separation of manganese from iron by means of pyridine.

When pyridine is added to a neutral solution of a manganous salt no precipitate is obtained. On warming, the solution slowly oxidises and the manganese begins to come down. The rate at which oxidation takes place, however, is about one-third as fast as the rate at which a manganous solution oxidises when treated with ammonium chloride and ammonium hydroxide under similar conditions. If the manganous solution is made acid with a little hydrochloric acid before addition of the pyridine to slight excess, the solution may then be heated for ten minutes without oxidation. Consequently, pyridine possesses considerable advantages over ammonium hydroxide in the separation under question, especially when a large amount of manganese is present. Practically, its only disadvantage is its cost. A very fair separation can be made with one precipitation.

On washing ferric hydroxide precipitated by pyridine, no iron at first appears in the filtrate. As the excess of pyridine is washed out of the precipitate, however, colloidal iron passes through the filter. On washing the precipitate with pyridine water (1 : 500) the iron is completely retained by the filter.

In the following experiments Merck's pyridine, "Medicinal grade," was used. It was re-distilled before using.

Pure iron wire was dissolved in 10 cc. of 4/N hydrochloric acid. A few drops of concentrated nitric acid were

added and the solution warmed to oxidise the iron. It was then diluted to 100 cc., warmed, and pyridine added from a burette. The precipitate was washed with pyridine water (1 : 500) :—

No.	Iron taken. Grm.	Iron found. Grm.
1.	0·0806	0·0807
2.	0·0823	0·0824
3.	0·0798	0·0810

In No. 1, the pyridine was added until the iron was just precipitated. In No. 2 there was an excess of 0·5 cc. of pyridine, and in No. 3 an excess of 1 cc.

Solutions of manganous chloride were then mixed in different proportions with ferric chloride. The amount of free acid was the same as was taken above. The precipitation takes place equally well in the cold or after gently warming. In the following series the manganese in the filtrate was not estimated, the object being to see what kind of a separation was made by a single precipitation. One-half a cubic centimetre in excess of pyridine was used in each case :—

No.	Iron taken. Grm.	Iron found. Grm.	Manganese present. Grm.
1.	0·0797	0·0798	0·1405
2.	0·0790	0·0792	0·0857
3.	0·0791	0·0792	0·0719
4.	0·0798	0·0802	0·0610

In the next series both the iron and manganese were estimated in order to see what effect the presence of the pyridine has on the precipitation of the manganese. The manganese cannot be completely precipitated by addition of bromine water to the hot solution. In addition, the formation of pyridine bromide interferes. In No. 1 the manganese was estimated in the usual manner by potassium carbonate. In Nos. 2, 3, and 4, chemically pure sodium hydroxide was used instead of the carbonate, the precipitation being made in porcelain basins :—

	Iron.		Manganese.	
No.	Taken. Grm.	Found. Grm.	Taken. Grm.	Found. Grm.
1.	0·0858	0·0862	0·0698	0·0691
2.	0·1136	0·1133	0·0667	0·0666
3.	0·1162	0·1155	0·2289	0·2285
4.	0·1268	0·1264	0·1145	0·1140

The conditions under which aluminium can be separated from manganese and aluminium and iron from beryllium by means of pyridine are under investigation.—*Journal of the American Chemical Society*, xxx., p. 593.

ON THE ESTIMATION OF CERIUM IN THE PRESENCE OF THE OTHER RARE EARTHS BY THE ACTION OF POTASSIUM FERRICYANIDE.

By PHILIP E. BROWNING and HOWARD E. PALMER.

THE work to be described was undertaken to determine how completely the oxidation of cerium from the cerous to the ceric condition may be effected by potassium ferricyanide in alkaline solution, and how completely the measure of the oxidation can be registered in the amount of potassium ferrocyanide formed, according to the following equation :—

$$2K_3FeC_6N_6 + Ce_2O_3 + 2KOH = 2K_4FeC_6N_6 + H_2O + 2CeO_2.$$

For this work a solution of pure cerous sulphate was made and standardised by precipitating measured and weighed portions with a definite amount of a standard solution of sodium oxalate, filtering, igniting the cerium oxalate, and weighing the ceric oxide obtained. As a check on this method, the excess of the sodium oxalate over the amount used for the precipitate was determined in the filtrate by titration with potassium permanganate, and this amount was subtracted from the whole amount of sodium oxalate used. From this result the cerium present can be readily estimated, the amount of sodium oxalate used in the precipitation being known (Browning and Lynch, *Journ. Am. Sci.*, 1899, [4], viii., 457).

The ferricyanide solution used was made by dissolving 2 grms. of carefully selected crystals of potassium ferricyanide in 100 cc. of water. About 20 cc. of this solution were used in each determination.

The procedure was as follows :—To measured and weighed portions of the cerous sulphate solution 20 cc. of the ferricyanide solution were added, and potassium hydroxide in solution to complete precipitation.

The precipitated hydroxide was filtered off, and the filtrate and washings, amounting in volume to from 200 cc. to 250 cc., after being made distinctly acid with dilute sulphuric acid, were titrated with a standard solution of potassium permanganate until the presence of the permanganate colour showed the oxidation of the ferrocyanide to the ferricyanide, according to the equation—

$$5K_4FeC_6N_6 + KMnO_4 + 4H_2SO_4 = 5K_3FeC_6N_6 + 3K_2SO_4 + MnSO_4 + 4H_2O$$

(Sutton's "Volumetric Analysis," Ninth Edition, p. 209). By this equation and the preceding one the amount of cerium present can be readily calculated.

Each day before the ferricyanide was used a portion of 20 cc. of the solution was acidified and titrated with the permanganate to colour, and the amount necessary, generally from one to three drops, was subtracted from the amount of the permanganate used in the actual determination. It is of interest to note that ferricyanide solutions kept in clear glass bottles for a week or more showed variations of only a drop or two in the amount of permanganate taken up.

TABLE I.

	Ce taken, calculated as Ce_2O_3. Grm.	Ce found, calculated as Ce_2O_3. Grm.	Error. Grm.
1.	0·1834	0·1819	−0·0015
2.	0·1376	0·1380	+0·0004
3.	0·1834	0·1829	−0·0005
4.	0·1834	0·1829	−0·0005
5.	0·1834	0·1834	—
6.	0·1376	0·1385	+0·0009
7.	0·1376	0·1371	−0·0005
8.	0·1376	0·1374	−0·0002
9.	0·1376	0·1380	+0·0004
10.	0·1834	0·1824	−0·0010
11.	0·1326	0·1335	+0·0009
12.	0·1326	0·1328	+0·0002

TABLE II.

	Ce taken, calculated as Ce_2O_3. Grm.	Ce found, calculated as Ce_2O_3. Grm.	Error. Grm.	Other rare earths present, calculated as oxides. Grm.
1.	0·1328	0·1335	+0·0007	0·1 ThO_2
2.	0·1327	0·1322	−0·0005	0·1 ,,
3.	0·0266	0·0275	+0·0009	0·1 ,,
4.	0·0267	0·0272	+0·0005	0·1 ,,
5.	0·1324	0·1326	+0·0002	0·1 Y_2O_3
6.	0·1326	0·1323	−0·0003	0·1 ,,
7.	0·0266	0·0264	−0·0002	0·1 ,,
8.	0·0264	0·0271	+0·0005	0·1 ,,
9.	0·1376	0·1370	−0·0006	0·15 $La_2O_3 + Di_2O_3$
10.	0·1101	0·1091	−0·0010	0·15 ,,
11.	0·1324	0·1332	+0·0008	0·03 ZrO_2

All the various operations in this process were carried on without warming the solution. The filtrations and washings were generally made under gentle pressure, and required on an average not more than fifteen to thirty minutes. In Table I. the results obtained with cerium present alone are given.

Solutions of the salts of the other rare earths, containing about 0·1 grm., were treated by the same method, and the failure to obtain evidence, by the permanganate, of the formation of potassium ferrocyanide, showed that there is no oxidation of these salts by the ferricyanide.

In Table II. the results obtained by estimating cerium according to this method in the presence of the other rare earths are given.

This method presents no difficulties in manipulation, and is especially adapted to the rapid estimation of cerium in rare earth mixtures.—*American Journal of Science*, xxvi., p. 83.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

PART III.—ANALYSIS OF THE ALUMINIUM AND IRON GROUPS, INCLUDING BERYLLIUM, URANIUM, VANADIUM, TITANIUM, ZIRCONIUM, AND THALLIUM.

By ARTHUR A. NOYES, WILLIAM C. BRAY, and ELLWOOD B. SPEAR.

(Continued from p. 94).

The Iron Group.

Procedure 61.—Transfer the Na_2O_2 precipitate (P. 52) to a casserole together with the filter if necessary, add 5—30 cc. HCl (1·12), boil gently till the precipitate is dissolved, filter to remove the paper, and evaporate the filtrate to 1 or 2 cc. To decompose the HCl add about 5 cc. HNO_3 (1·42), and boil as long as oxides of nitrogen are given off. Add 5—20 cc. HNO_3 (1·42), heat to boiling, add about 0·5 grm. of solid $KClO_3$ and boil gently, adding more $KClO_3$ in small portions if a large precipitate forms. (Dark brown or black precipitate, presence of *manganese*). Boil gently for a minute or two, and filter through an asbestos filter, made by pouring a suspension of washed asbestos over a compact wad of glass-wool in a glass funnel. (See Note 4). Heat the filtrate to boiling, add more $KClO_3$, boil, and filter through the same filter if more of the precipitate separates. Wash two or three times with HNO_3 (1·42) which has previously been freed from the oxides of nitrogen by warming with a little $KClO_3$. Evaporate the filtrate to about 5 cc., but not further, dilute to 20 or 30 cc., and filter the solution if it is turbid. (Precipitate, P. 62; filtrate, P. 63).

Notes.

1. HCl is used for dissolving the Na_2O_2 precipitate rather than HNO_3. Pure concentrated HNO_3 does not dissolve hydrated MnO_2 except in the presence of filter-paper, whereby the HNO_3 is reduced to lower oxides; the action is more rapid with HCl (for the MnO_2 is thereby quickly reduced to manganous chloride with evolution of chlorine).

2. By $HClO_3$ in HNO_3 solution (but not by HNO_3 alone) manganous salts are rapidly oxidised to hydrated MnO_2 with formation of chlorine dioxide (ClO_2), which escapes as a yellow gas. The HCl must previously be completely removed by evaporation and boiling with HNO_3, since the oxides of nitrogen resulting from its action on the HNO_3 would continuously dissolve the precipitate.

3. The separation of manganese in this way from the other metals of this group is entirely satisfactory with the following exceptions. A small quantity of iron (up to 1 mgrm.) may be completely carried down with a large quantity (500 mgrms.) of manganese. The same is true in a much higher degree of titanium, of which even 50 mgrms. may be entirely precipitated with 500 mgrms. of manganese. Much zirconium is also carried down, but never quite completely. Provision is therefore made (in *P. 62*a*) for the detection of these three elements in the precipitate (if it is large) as well as in the filtrate. If it is not thought necessary to test for zirconium in the precipitate, the certain detection of titanium can be much more quickly accomplished just before precipitating the manganese, by diluting the HNO_3 solution, from which the HCl has been removed, with once or twice its volume of water, and adding 3 cc. of 3 per cent H_2O_2 solution. An orange-yellow or orange-red colour shows the presence of titanium. (See *P. 65*b*, N. 1). In the absence of HCl iron does not interfere with this test, nor does even a large quantity of nickel or cobalt prevent a distinct change of colour from being seen.

4. In filtering the MnO_2 a cylindrical glass funnel with a small delivery tube is usually employed in quantitative analysis. An ordinary conical funnel is, however, satisfactory, provided the wad of glass-wool is made compact and enough asbestos is used. Filtration will, to be sure, be slow if the glass-wool is packed very tightly or if the asbestos mat is very thick, but in that case suction may be applied.

5. On evaporating the HNO_3 filtrate, titanium and zirconium oxides may separate out, especially if the solution be evaporated almost to dryness. For this reason the solution is evaporated only to about 5 cc., but even then a small white precipitate will sometimes be obtained when these elements are present in large amount.

Procedure 62.—Transfer the whole of the $HClO_3$ precipitate (P. 61) if it is small (containing less than 5 mgrms. Mn), or 5—10 mgrms. of it if it is large, to a casserole; add 1 or 2 grms. solid PbO_2 and about 10 cc. HNO_3 (1·20); boil for about two minutes in a casserole covered with a watch-glass; pour the mixture into a test-tube, and allow the PbO_2 to settle. (Violet-red solution, presence of *manganese*).

If the precipitate is large, dissolve the remainder in hot HCl (1·12) in a casserole, or by pouring a 10—15 cc. portion repeatedly through the filter, and boil the solution to expel chlorine. To one-tenth of this solution add 5 cc. KCNS solution. (Deep red colour, presence of *iron*). Treat the remainder of the HCl solution by *P. 62*a* to recover any titanium and zirconium that may be present.

Notes.

1. This confirmatory test for manganese is usually superfluous since the precipitation of MnO_2 by $HClO_3$ is highly characteristic. In order that the PbO_2 test may be satisfactory, the HNO_3 used must be fairly concentrated and the boiling continued for two or three minutes.

Procedure 62*a*.—To the HCl solution (P. 62), without evaporating it, add NH_4OH (0·96) until the mixture is barely alkaline, avoiding the addition of more than two or three drops in excess; heat nearly to boiling for two or three minutes, filter at once, and wash with hot water. Reject the filtrate. Dissolve the precipitate in a little hot HCl (1·12) (without diluting it with water), reserve it, and unite it with the main HCl solution to be treated in *P. 65*a*.

Notes.

1. In order to avoid as far as possible the precipitation of manganese by NH_4OH, the OH^- concentration is kept small by avoiding an excess of NH_4OH and by having a large quantity of ammonium salt present. Under these conditions the oxidation by the air to the manganic state is slow. If, however, much NH_4OH be added, oxidation takes place rapidly and much

* From the *Journal of the American Chemical Society*, xxx., No. 4.

manganese may be precipitated as $Mn(OH)_3$, yielding a brown precipitate. Even at best a little manganese will come down, but a moderate amount does not interfere with the subsequent tests for titanium and zirconium.

Procedure 63.—Add about one-tenth of the HNO_3 solution (P. 61) to three or four times its volume of ammonium molybdate reagent, and heat to 60—70°. (Yellow, finely crystalline precipitate, presence of *phosphate*). If there is no precipitate, or only a very small one, treat the remainder of the HNO_3 solution by P. 64; otherwise by P. 65.

Notes.

1. Phosphate is tested for at this point because a different treatment is necessary when it is present in significant amount, in order to separate from it alkaline-earth elements and to provide for their detection. When phosphate is not present, iron, thallium, titanium, and zirconium can be separated from nickel, cobalt, and the alkaline-earth elements by NH_4OH (as in P. 64); but, when considerable phosphate is present, the alkaline-earth elements would be partly or wholly precipitated in combination with it. (See P. 51, N. 6).

2. In order that the phosphate test may be delicate and may appear immediately, a large proportion of the molybdate reagent must be used and the solution must be warmed. The precipitate of ammonium phospho-molybdate is of complicated and somewhat variable composition; it contains ammonium phosphate and molybdic acid, approximately in the proportion $(NH_4)_3PO_4 : 12MoO_3$.

Procedure 64.—If phosphate is absent, make the HNO_3 solution (P. 62) strongly alkaline with NH_4OH (0·96) using an excess of 3—5 cc. (Dark red precipitate, presence of *iron*). Filter, and wash the precipitate, using suction if the precipitate is large, and sucking it as dry as possible. Treat the filtrate by P. 66.

Dissolve the precipitate in HCl (1·12), warming if necessary, taking care not to dilute the acid by wash water. To about one-tenth of the solution add 5 cc. KCNS solution. (Dark red colour, presence of *iron*). *Treat the remainder of the solution by *P. 65*a*.

Notes.

1. If titanium and zirconium are to be tested for, it is important to dissolve the NH_4OH precipitate in HCl of a specific gravity 1·12 (24 per cent HCl) and to avoid dilution, for the separation in *P. 65*a* depends on the concentration of the HCl.

2. The red colour obtained on adding KCNS is due to the formation of un-ionised ferric thiocyanate, $Fe(CNS)_3$. This test may be made in the presence of much HCl, for the acid HCNS is also a highly dissociated acid, which is therefore not displaced from its salt. Much HNO_3 must not, however, be present; for, by its action on KCNS, NO_2 may be formed, and this also gives a deep red colour with KCNS. This test for iron is an extremely delicate one; and if only a faint colour is obtained, the acids used in the process must be tested for iron.

(To be continued).

MISCELLANEOUS.

Preparation of a Solution for Making Standard Solutions of Sodium Hydroxide.—H. W. Cowles, Jun. —Prepare an approximately 50 per cent solution of sodium hydroxide by dissolving 50 grms. of ordinary chemically pure caustic soda sticks in 50 cc. of distilled water and leave tightly stoppered over night. The major portion of the impurities is insoluble in such a concentrated solution. The next day the proper amount of the clear supernatant solution is weighed or measured out, as most convenient, and diluted to the mark with freshly boiled distilled water. Theoretically 8 grms. or 5·25 cc. are required per litre of N/10 solution, but owing to the impurities which have settled out it is safer to use 8·5 grms. or 5·75 cc. per litre, and then standardise against N/10 acid. With such a standard solution, made up as directed and kept in an automatic burette with a potash bulb to purify the air that enters the apparatus, the strength is maintained indefinitely, while one drop of N/10 H_2SO_4 is more than sufficient to render 25 cc. of the solution, already neutralised to phenolphthalein, acid to methyl orange, showing that it is practically completely free from carbonates, &c. In proof of this, barium hydroxide gives no precipitate when added to 25 cc. of the solution. The remainder of the strong caustic soda solution, if kept tightly stoppered, will furnish material for the preparation of future supplies when needed.—*Journal of the American Chemical Society*, xxx., No. 7.

The Iron and Steel Institute.—President, Sir Hugh Bell, Bart.—In accordance with previous announcements, the Autumn Meeting of the Iron and Steel Institute will be held at Middlesbrough on Monday, Tuesday, Wednesday, Thursday, and Friday, September 28th, 29th, and 30th, October 1st and 2nd, 1908. An influential Reception Committee has been formed, with the Worshipful the Mayor of Middlesbrough (Lieut.-Colonel T. G. Poole, V.D.) as Chairman, and Mr. John H. Amos (Queen's Terrace, Middlesbrough) as Hon. Secretary. The following papers have been offered for reading:—

"Scientific Control of Fuel Supply." By Prof. H. E. Armstrong, Ph.D., LL.D., F.R.S. (London).
"Metallurgy at the Franco-British Exhibition." By H. Bauerman, Hon. Member.
"Gas Producer Practice." By Prof. W. A. Bone, D.Sc., F.R.S. (Leeds), and R. V. Wheeler, D.Sc. (Normanton).
"Constitution of Carbon Steels." By Prof. E. D. Campbell (Ann Arbor, Michigan, U.S.A.).
"Freezing-point of Iron." By Prof. H. C. H. Carpenter, M.A., Ph.D. (Manchester).
"Production of Finished Iron Sheets and Tubes in One Operation." By S. O. Cowper-Coles (London).
"Chemical Control of the Basic Open-Hearth Process." By Alfred Harrison (Warrington), and R. V. Wheeler, D.Sc. (Normanton).
"Mechanical Cleaning of Iron Ores." By T. C. Hutchinson (Middlesbrough).
"Messrs. Bell Brothers' Blast Furnaces, from 1844 to 1908." By Greville Jones (Middlesbrough).
"Influence of Silicon on the Physical and Chemical Properties of Pig-iron." By A. Jouve (Paris).
"Some Results of Experience with Electrically Driven Rolling Mills." By C. Koettgen (London), and C. A. Ablett, B.Sc. (London).
"Electric Power Supply." By Charles H. Merz (London).
"Future Development of the Metal Mixer." By A. E. Pratt, Assoc.R.S.M. (London).
"Test for Ascertaining the Relative Wearing Properties of Steel Rails." By E. H. Saniter (Rotherham).
"Workshop Microscope." By J. E. Stead, F.R.S. (Member of Council).
"Analysis and Synthesis in the Foundry." By J. E. Stead, F.R.S. (Member of Council), and T. Westgarth (Middlesbrough).

Members who intend to take part in the discussion will, on notifying such intention to the Secretary, have copies of the papers forwarded to them a week in advance, as far as that may be possible.

The Owners of British Patent No. 29130/04, entitled "Improvements in the Manufacture of Sizing or Finishing Media," are desirous of disposing of the patent or entering into a working arrangement with firms likely to be interested in the same. The patent covers an invention interesting to manufacturers of Sizing or Finishing Media and to Wall-paper manufacturers and Decorators.—Full particulars can be obtained from, and offers made (for transmission to the Owners) to, MARKS and CLERK, 18, Southampton Buildings, Chancery Lane, London, W.C.

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BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Dublin, 1908.

INAUGURAL ADDRESS OF THE PRESIDENT,

Francis Darwin, M.A., Ph.D., LL.D., F.R.S.

Before entering on the subject of my Address, I may be allowed to refer to the loss which the British Association has sustained in the death of Lord Kelvin. He joined the Association in 1847, and had been for more than fifty years a familiar figure at our meetings. This is not the occasion to speak of his work in the world or of what he was to his friends, but rather of his influence on those who were personally unknown to him. It seems to me characteristic of him that something of his vigour and of his personal charm was felt far beyond the circle of his intimate associates, and many men and women who never exchanged a word with Lord Kelvin, and are in outer darkness as to his researches, will miss his genial presence and feel themselves the poorer to-day. By the death of Sir John Evans the Association is deprived of another faithful friend. He presided at Toronto in 1897, and since he joined the Association in 1861 had been a regular attendant at our meetings. The absence of his cheerful personality and the loss of his wise counsels will be widely felt.

May I be permitted one other digression before I come to my subject? There has not been a Botanical President of the British Association since the Norwich meeting forty years ago, when Sir Joseph Hooker was in the chair, and in "eloquent and felicitous words" (to quote my father's letter) spoke in defence of the doctrine of evolution. I am sure that every member of this Association will be glad to be reminded that Sir Joseph Hooker is, happily, still working at the subject that his lifelong labours have so greatly advanced, and of which he has long been recognised as the honoured chief and leader.

You will perhaps expect me to give a retrospect of the progress of evolution during the fifty years that have elapsed since July 1, 1858, when the doctrine of the origin of species by means of natural selection was made known to the world in the words of Mr. Darwin and Mr. Wallace. This would be a gigantic task, for which I am quite unfitted. It seems to me, moreover, that the first duty of your President is to speak on matters to which his own researches have contributed. My work—such as it is—deals with the movements of plants, and it is with this subject that I shall begin. I want to give you a general idea of how the changes going on in the environment act as stimuli and compel plants to execute certain movements. Then I shall show that what is true of those temporary changes of shape we describe as movements is also true of the permanent alterations known as morphological.

I shall insist that, if the study of movement includes the problem of stimulus and reaction, morphological change must be investigated from the same point of view. In fact, that these two departments of inquiry must be classed together, and this, as we shall see, has some important results—namely, that the dim beginnings of habit or unconscious memory that we find in the movements of plants and animals must find a place in morphology; and inasmuch as a striking instance of correlated morphological changes is to be found in the development of the adult from the ovum, I shall take this ontogenetic series and attempt to show you that here also something equivalent to memory or habit reigns.

Many attempts have been made to connect in this way the phenomena of memory and inheritance, and I shall ask you to listen to one more such attempt, even though I am forced to appear as a champion of what some of you consider a lost cause—the doctrine of the inheritance of acquired characters.

Movement.

In his book on "The Power of Movement in Plants," 1880, p. 571, my father wrote that "it is impossible not to be struck with the resemblance between the foregoing movements of plants and many of the actions performed unconsciously by the lower animals." In the previous year Sachs ("Arbeiten, 1879, ii., p. 282) had in like manner called attention to the essential resemblance between the irritability of plants and animals. I give these statements first because of their simplicity and directness; but it must not be forgotten that before this Pfeffer had begun to lay down the principles of what is now known as *Reizphysiologie*, or the physiology of stimulus, for which he and his pupils have done so much ("Osmotische Untersuchungen," 1877, p. 202).

The words of Darwin which I have quoted afford an example of the way in which science returns to the obvious. Here we find revived, in a rational form, the point of view of the child or of the writer of fairy stories. We do not go so far as the child; we know that flowers do not talk or walk; but the fact that plants must be classed with animals as regards their manner of reaction to stimuli has now become almost a commonplace of physiology. And inasmuch as we ourselves are animals, this conception gives us a certain insight into the reactions of plants which we should not otherwise possess. This is, I allow, a very dangerous tendency, leading to anthropomorphism, one of the seven deadly sins of science. Nevertheless, it is one that must be used unless the great mass of knowledge accumulated by psychologists is to be forbidden ground to the physiologist.

Jennings has admirably expressed the point of view from which we ought to deal with the behaviour of the simpler organisms ("The Behaviour of the Lower Organisms," 1904, p. 124). He points out that we must study their movements in a strictly objective manner: that the same point of view must be applied to man, and that any resemblance between the two sets of phenomena are not only an allowable but a necessary aid to research.

What, then, are the essential characters of stimuli and of the reactions which they call forth in living organisms? Pfeffer has stated this in the most objective way. An organism is a machine which can be set going by touching a spring or trigger of some kind; a machine in which energy can be set free by some kind of releasing mechanism. Here we have a model of at least some of the features of reaction to stimulation.

The energy of the cause is generally out of all proportion to the effect, *i.e.*, a small stimulus produces a big reaction. The specific character of the result depends on the structure of the machine rather than on the character of the stimulus. The trigger of a gun may be pulled in a variety of different ways without affecting the character of the explosion. Just in the same way a plant may be made to curve by altering its angle to the vertical, by lateral illumination, by chemical agency, and so forth; the curvature is of the same nature in all cases, the release-action differs. One of those chains of wooden bricks in which each knocks over the next may be set in action by a touch, by throwing a ball, by an erring dog, in short by anything that upsets the equilibrium of brick No. 1; but the really important part of the game, the way in which the wave of falling bricks passes like a prairie fire round a group of Noah's Ark animals, or by a bridge over its own dead body and returns to the starting-point, &c.—these are the result of the magnificent structure of the thing as a whole, and the upset of brick No. 1 seems a small thing in comparison.

For myself I see no reason why the term *stimulus* should not be used in relation to the action of mechanisms in general; but by a convention which it is well to respect

stimulation is confined to the protoplasmic machinery of living organisms.

The want of proportion between the stimulus and the reply, or, as it has been expressed, the unexpectedness of the result of a given stimulus, is a striking feature in the phenomena of reaction. That this should be so need not surprise us. We can, as a rule, only know the stimulus and the response, while the intermediate processes of the mechanism are hidden in the secret life of protoplasm. We might, however, have guessed that big changes would result from small stimuli, since it is clear that the success of an organism in the world must depend partly at least on its being highly sensitive to changes in its surroundings. This is the adaptive side of the fundamental fact that living protoplasm is a highly unstable body. Here I may say one word about the adaptation as treated in the "Origin of Species." It is the present fashion to minimise or deny altogether the importance of natural selection. I do not propose to enter into this subject; I am convinced that the inherent strength of the doctrine will insure its final victory over the present anti-Darwinian stream of criticism. From the Darwinian point of view it would be a remarkable fact if the reactions of organisms to natural stimuli were not adaptive. That they should be so, as they undoubtedly are, is not surprising. But just now I only call attention to the adaptive character of reactions from a descriptive point of view.

Hitherto I have implied the existence of a general character in stimulation without actually naming it; I mean the indirectness of the result. This is the point of view of Dutrochet, who in 1824 said that the environment suggests but does not directly cause the reaction. It is not easy to make clear in a few words the conception of indirectness. Pfeffer ("Physiology," Engl. edit., i., p. 11) employs the word *induction*, and holds that external stimuli act by producing internal change, such changes being the link between stimulus and reaction. It may seem, at first sight, that we do not gain much by this supposition; but since these changes may be more or less enduring, we gain at least the conception of *after effect* as a quality of stimulation. What are known as *spontaneous* actions must be considered as due to internal changes of unknown origin.

It may be said that in speaking of the "indirectness" of the response to stimuli we are merely expressing in other words the conception of release-action; that the explosion of a machine is an indirect reply to the touch on the trigger. This is doubtless true, but we possibly lose something if we attempt to compress the whole problem into the truism that the organism behaves as it does because it has a certain structure. The quality of indirectness is far more characteristic of an organism than of a machine, and to keep it in mind is more illuminating than a slavish adherence to the analogy of a machine. The reaction of an organism depends on its past history; but, it may be answered, this is also true of a machine the action of which depends on how it was made, and in a less degree on the treatment it has received during use. But in living things this last feature in behaviour is far more striking, and in the higher organisms past experience is all-important in deciding the response to stimulus. The organism is a plastic machine profoundly affected in structure by its own action, and the unknown process intervening between stimulus and reaction (on which the indirectness of the response depends) must have the fullest value allowed it as a characteristic of living creatures.

For the zoological side of biology a view similar to that of Pfeffer has been clearly stated by Jennings in his admirable studies on the behaviour of infusoria, rotifers, &c. ("Contributions to the Study of the Behaviour of the Lower Organisms," Carnegie Institution, 1904, p. 111). He advances strong arguments against the theories of Loeb and others, according to which the stimulus acts directly on the organs of movement; a point of view which was formerly held by botanists, but has since given place to the conception of the stimulation acting on the organism as a whole. Unfortunately for botanists these movements are by the zoologists called *tropisms*, and are thus liable to be confused with the geotropism, heliotropism, &c., of plants; to these movements, which are not considered by botanists to be due to direct action of stimuli, Loeb's assumptions do not seem to be applicable.

Jennings's position is that we must take into consideration what he calls "physiological state, *i.e.*, 'the varying internal physiological conditions of the organisms, as distinguished from permanent anatomical conditions.'" Though he does not claim novelty for his view, I am not aware that it has ever been so well stated. External stimuli are supposed to act by altering this physiological state; that is, the organism is temporarily transformed into what, judged by its reactions, is practically a different creature.

This may be illustrated by the behaviour of *Stentor*, one of the fixed infusoria (Jennings, "Behaviour of the Lower Organisms," 1906, p. 170). If a fine jet of water is directed against the disc of the creature, it contracts "like a flash" into its tube. In about half a minute it expands again, and the cilia resume their activity. Now we cause the current to act again upon the disc. This time the *Stentor* does not contract, which proves that the animal has been in some way changed by the first stimulus. This is a simple example of "physiological state." When the *Stentor* was at rest, before it received the first current of water, it was in state 1, the stimulus changed state 1 into state 2, to which contraction is the reaction. When again stimulated it passed into state 3, which does not produce contraction.

We cannot prove that the contraction which occurred when the *Stentor* was first stimulated was due to a change of state. But it is a fair deduction from the result of the whole experiment, for after the original reaction the creature is undoubtedly in a changed state, since it no longer reacts in the same way to a repetition of the original stimulus.

Jennings points out that, as in the case of plants, spontaneous acts are brought about when the physiological state is changed by unknown causes, whereas in other cases we can point to an external agency by which the same result is effected.

Morphological Changes.

Let us pass on to the consideration of the permanent or morphological changes, and the stimuli by which they are produced, a subject to which, in recent years, many workers have devoted themselves. I need only mention the names of Vöchting, Goebel, and Klebs among botanists, and those of Loeb, Herbst, and Driesch among zoologists, to remind you of the type of research to which I refer.

These morphological alterations produced by changes in environment have been brought under the rubric of reaction to stimulation, and must be considered as essentially similar to the class of temporary movements of which I have spoken.

The very first stage in development may be determined by a purely external stimulus. Thus the position of the first cell-wall in the developing spore of *Equisetum*, is determined by the direction of incident light (Stahl, *Ber. d. Bot. Ges.*, 1885, p. 334). In the same way the direction of light settles the plane of symmetry of *Marchantia* as it develops from the gemma (Pfeffer, in Sachs' "Arbeiten," i., p. 92). But the more interesting cases are those where the presence or absence of a stimulus makes an elaborate structural difference in the organism. Thus, as Stahl has shown (*Jenaische Zeit.*, 1883, p. 162), beech leaves developed in the deep shade of the middle of the tree are so different in structure from leaves grown in full sunlight that they would unhesitatingly be described as belonging to different species. Another well-known case is the development of the scale-leaves on the rhizome of *Circæa* into the foliage leaves under the action of light (Goebel in *Bot. Zeitung*, 1880).

The power which the experimenter has over the lower plants is shown by Klebs, who kept *Saprolegnia mixta*, a fungus found on dead flies, in uninterrupted vegetative growth for six years; while by removing a fragment of the plant and cultivating it in other conditions the reproductive organs could at any time be made to appear ("Willkürliche Entwick.," p. 27).

Chlamydomonas media, a unicellular green alga, when grown in a 0·4 per cent nutrient solution, continues to increase by simple division, but conjugating gametes are formed in a few days if the plant is placed in pure water, and kept in bright light (Klebs, "Bedingungen," 1896, p. 430). Numberless other cases could be given of the regulation of form in the lower organisms. Thus, *Sporodinia* grown on peptone-gelatine produces sporangiferous hypha, but on sugar zygotes are formed. Again, *Protosiphon botryoides*, if grown on damp clay, can most readily be made to produce spores by transference to water either in light or in darkness. But for the same plant cultivated in Knop's solution the end can best be obtained by placing the culture in the dark (*Biol. Centralbl.*, 1904, pp. 451—3). Still these instances of the regulation of reproduction are not so interesting from our point of view as some of Klebs' later results (*Jahrb. f. wiss. Bot.*, 1906, xlii., p. 162). Thus he has shown that the colour of the flower of *Campanula trachelium* can be changed from blue to white and back again to blue by varying the conditions under which the plant is cultivated. Again, with *Sempervivum* he has been able to produce striking results —*e.g.*, the formation of apetalous flowers with one instead of two rows of stamens (*Abhandl. Naturforsch. Ges. zu Halle*, 1906, xxv., pp. 31, 34, &c.). Diminution in the number of stamens is a common occurrence in his experimental plants, and absolute loss of these organs also occurs. Many other abnormalities were induced, both in the stamens and in other parts of the flowers.

There is nothing new in the character of these facts*; what has been brought to light (principally by the work of Klebs) is the *degree* to which ontogeny is controllable. We are so much in the habit of thinking of the stable element in ontogeny that the work of Klebs strikes us with something of a shock. Most people would allow that change of form is ultimately referable to changed conditions, but many of us were not prepared to learn the great importance of external stimuli in ontogeny.

Klebs begins by assuming that every species has a definite *specific structure*, which he compares to chemical character. Just as a substance such as sulphur may assume different forms under different treatment, so he assumes that the specific structure of a plant has certain potentialities which may be brought to light by appropriate stimuli. He divides the agencies affecting the structure into external and internal conditions, the external being supposed to act by causing alterations in the internal conditions.

It will be seen that the scheme is broadly the same as that of Pfeffer for the case of the movement and other temporary reactions. The internal conditions of Klebs correspond also to the "physiological state" of Jennings.

From what has gone before, it will be seen that the current conception of stimulus† is practically identical whether we look at the phenomena of movement or those of structure. If this is allowable—and the weight of evidence is strongly in its favour—a conclusion of some interest follows.

If we reconsider what I have called the indirectness of stimulation, we shall see that it has a wider bearing than is at first obvious. The "internal condition" or "physiological state" is a factor in the regulation of the organism's action, and it is a factor which owes its character to external agencies which may no longer exist.

The fact that stimuli are not momentary in effect, but leave a trace of themselves on the organism is, in fact, the physical basis of the phenomena grouped under memory in its widest sense as indicating that action is regulated by past experience. Jennings remarks (*loc. cit.*, 1904, p. 124): —"In the higher animals, and especially in man, the essential features in behaviour depend very largely on the history of the individual; in other words, upon the present physiological condition of the individual, as determined by the stimuli it has received and the reactions it has performed. But in this respect the higher animals do not differ in principle, but only in degree, from the lower organisms . . . ." I venture to believe that this is true of plants as well of animals, and that it is further broadly true not only of physiological behaviour, but of the changes that are classed as morphological.

Semon in his interesting book, "Die Mneme,"* has used the word *Engram* for the trace or record of a stimulus left on the organism. In this sense we may say that the internal conditions of Pfeffer, the physiological states of Jennings, and the internal conditions of Klebs are, broadly speaking, *Engrams*. The authors of these theories may perhaps object to this sweeping statement, but I venture to think it is broadly true.

The fact that in some cases we recognise the chemical or physical character of the internal conditions does not by any means prevent our ascribing a *mnenic* memory-like character to them, since they remain causal agencies built up by external conditions which have, or may have, ceased to exist. Memory will be none the less memory when we know something of the chemistry and physics of its neutral concomitant.

Habit illustrated by Movement.

In order to make my meaning plain as to the existence of a *mnemic* factor in the life of plants, I shall for the moment leave the morphological side of life and give an instance of habitual movement.

Sleeping plants are those in which the leaves assume at night a position markedly different from that shown by day. Thus the leaflets of the scarlet-runner (*Phaseolus*) are more or less horizontal by day and sink down at night. This change of position is known to be produced by the alternation of day and night. But this statement by no means exhausts the interest of the phenomenon. A sensitive photographic plate behaves differently in light and darkness; and so does a radiometer, which spins by day and rests at night.

If a sleeping-plant is placed in a dark room after it has gone to sleep at night, it will be found next morning in the light-position, and will again assume the nocturnal position as evening comes on. We have, in fact, what seems to be

* See the great collection of facts illustrating the "direct and definite action of the external conditions of life" in "Variation of Animals and Plants," ii., 271).

† With regard to the terminology of stimulation, I believe that it would greatly simplify matters if our classification of casual conditions could be based on the relation of the nucleus to the rest of the cell. But our knowledge does not at present allow of more than a tentative statement of such a scheme. It is now widely believed that the nucleus is the bearer of the qualities transmitted from generation to generation, and the regulator of ontogeny. May we not therefore consider it probable that the nucleus plays in the cell the part of a central nervous system? In plants there is evidence that the ectoplasm is the sensitive region, and, in fact, plays the part of the cell's sense-organ. The change that occurs in the growth of a cell, as a response to stimulus, would on this scheme be a reflex action dependent for its character on the structure of the nucleus. The "indirectness" of stimulation would then depend on the reception by the nucleus of the excitation set up in the ectoplasm, and the secondary excitation reflected from the nucleus, leading to certain changes in the growth of the cell. If the nucleus be the bearer of the past history of the individual, the scheme here sketched would accord with the adaptive character of normal reactions, and would fall into line with what we know of the regulation of actions in the higher organisms. Pfeffer ("Physiology of Plants," Eng. trans., iii., 101) has briefly discussed the possibility of thus considering the nucleus as a reflex centre, and has pointed out difficulties in the way of accepting such a view as universally holding good. Delage ("L'Hérédite," 2nd Edit., 1903, p. 88) gives a good summary of the evidence which induces him to deny the mastery of the cell by the nucleus. Driesch, however ("Analytische Theorie der organischen Entwicklung," 1894, p. 81), gives reasons for believing that the cytoplasm is the receptive region, while the nucleus is responsible for the reaction, and it is on this that he bases his earlier theory of ontogeny.

* "Die Mneme, als erhaltendes Prinzip im Wechsel des organischen Geschehens," von Richard Semon, 1te Auflage, Leipzig, 1904, 2te Auflage, 1908. It is a pleasure to express my indebtedness to this work, as well as for the suggestions and criticisms which I owe to Professor Semon personally.

a habit built by the alternation of day and night. The plant normally drops its leaves at the stimulus of darkness and raises them at the stimulus of light. But here we see the leaves rising and falling in the absence of the accustomed stimulation. Since this change of position is not due to external conditions it must be the result of the internal conditions which habitually accompany the movement. This is the characteristic *par excellence* of habit—namely, a capacity, acquired by repetition, of reacting to a fraction of the original environment. We may express it in simpler language. When a series of actions are compelled to follow each other by applying a series of stimuli they become organically tied together, or *associated*, and follow each other automatically, even when the whole series of stimuli are not acting. Thus in the formation of habit *post hoc* comes to be equivalent to *propter hoc*. Action B automatically follows action A, because it has repeatedly been compelled to follow it.

This may be compared with Herbert Spencer's description of an imaginary case ("Psychology," 2nd edit., 1870, vol. i., p. 435), that of a simple aquatic animal which contracts its tentacles on their being touched by a fish or a bit of seaweed washed against it. If such a creature is also sensitive to light the circumstances under which contraction takes place will be made up of two stimuli—those of light and of contact—following each other in rapid succession. And, according to the above statement of the essential character of associative habit, it will result that the light-stimulus alone may suffice, and the animal will contract without being touched.

Jennings ("Behaviour of the Lower Organisms," 1906, p. 289) has shown that the basis of memory by association exists in so low an organism as the infusorian *Stentor*. When the animal is stimulated by a jet of water containing carmine in suspension, a physiological state A is produced, which, however, does not immediately lead to a visible reaction. As the carmine stimulus is continued or repeated, state B is produced, to which the *Stentor* reacts by bending to one side. After several repetitions of the stimulus, state C is produced, to which the animal responds by reversing its ciliary movement, and C finally passes into D, which results in the *Stentor* contracting into its tube. The important thing is that after many repetitions of the above treatment the organism "contracts at once as soon as the carmine comes in contact with it." In other words, states B and C are apparently omitted, and A passes directly into D, *i.e.*, into the state which gives contraction as a reaction. Thus we have in an infusorian a case of short-circuiting precisely like the case which has been quoted from Herbert Spencer as illustrating association. But Jennings' case has the advantage of being based on actual observation. He generalises the result as the "law of the resolution of physiological states" in the following words:—"The resolution of one physiological state into another becomes easier and more rapid after it has taken place a number of times." He goes on to point out that the operation of this law is seen in the higher organisms, "in the phenomena which we commonly call memory, association, habit-formation, and learning."

In spite of this evidence of mnemic power in the simplest of organisms, objections will no doubt be made to the statement that association of engrams can occur in plants.

Pfeffer, whose authority none can question, accounts for the behaviour of sleeping-plants principally on the more general ground that when any movement occurs in a plant there is a tendency for it to be followed by a reversal—a swing of the physiological pendulum in the other direction. Pfeffer* compares it to a released spring which makes several alternate movements before it settles down to equilibrium. But the fact that the return movements occur at the same time-intervals as the stimuli is obviously the striking feature of the case. If the pendulum-like swing always tended to occur naturally in a twelve hours' rhythm it would be a different matter. But Pfeffer has shown that a rhythm of six hours can equally well be built up. And the experiments of Miss Pertz and myself ("Annals of Botany," 1892 and 1903) show that a half-hourly or quarter-hourly rhythm can be produced by alternate geotropic stimulation.

We are indebted to Keeble (Gamble and Keeble, *Q. J. Mic. Science*, xlvii., p. 401) for an interesting case of apparent habit among the lower animals. *Convoluta roscoffensis*, a minute wormlike creature found on the coast of Brittany, leads a life dependent on the ebb and flow of the sea. When the tide is out the *Convoluta* come to the surface, showing themselves in large green patches. As the rising tide begins to cover them they sink down into safer quarters. The remarkable fact is that when kept in an aquarium, and therefore removed from tidal action, they continue for a short time to perform rhythmic movements in time with the tide.

Let us take a human habit, for instance that of a man who goes a walk every day and turns back at a given mile-post. This becomes habitual, so that he reverses his walk automatically when the limit is reached. It is no explanation of the fact that the stimulus which makes him start from home includes his return—that he has a mental return-ticket. Such explanation does not account for the point at which he turns, which as a matter of fact is the result of association. In the same way a man who goes to sleep will ultimately wake; but the fact that he wakes at four in the morning depends on a habit built up by his being compelled to rise daily at that time. Even those who will deny that anything like association can occur in plants cannot deny that in the continuance of the nyctitropic rhythm in constant conditions we have, in plants, something which has general character of habit, *i.e.*, a rhythmic action depending on a rhythmic stimulus that has ceased to exist.

On the other hand, many will object that even the simplest form of association implies a nervous system. With regard to this objection it must be remembered that plants have two at least of the qualities characteristic of animals—namely, extreme sensitiveness to certain agencies and the power of transmitting stimuli from one part to another of the plant body. It is true that there is no central nervous system, nothing but a complex system of nuclei; but these have some of the qualities of nerve cells, while intercommunicating protoplasmic threads may play the part of nerves. Spencer ("Psychology," 2nd edit., vol. i., p. 615) bases the power of association on the fact that every discharge conveyed by a nerve "leaves it in a state for conveying a subsequent like discharge with less resistance." Is it not possible that the same thing may be as true of plants as it apparently is of infusoria? We have seen reasons to suppose that the "internal conditions" or "physiological states" in plants are of the nature of engrams, or residual effects of external stimuli, and such engrams may become associated in the same way.

There is likely to be another objection to my assumption that a simple form of associated action occurs in plants—namely, that association implies consciousness. It is impossible to know whether or not plants are conscious; but it is consistent with the doctrine of continuity that in all living things there is something psychic, and if we accept this point of view we must believe that in plants there exists a faint copy of what we know as consciousness in ourselves (see James Ward, "Naturalism and Agnosticism," vol. i., Lecture X.).

I am told by psychologists that I must define my point of view. I am accused of occupying that unscientific position known as "sitting on the fence." It is said that, like other biologists, I try to pick out what suits my purpose from two opposite schools of thought—the psychological and the physiological.

What I claim is that, as regards reaction to environment, a plant and a man must be placed in the same great class, in spite of the obvious fact that as regards complexity of behaviour the difference between them is enormous. I am

* See Pfeffer, *Abhandl. K. Sachs. Ges.*, Bd. xxx., 1907. It is impossible to do justice to Pfeffer's point of view in the above brief statement.

not a psychologist, and I am not bound to give an opinion as to how far the occurrence of definite actions in response to stimulus is a physiological and how far a psychological problem. I am told that I have no right to assume the neural series of changes to be the cause of the psychological series, though I am allowed to say that neural changes are the universal concomitants of psychological change. This seems to me, in my ignorance, an unsatisfactory position. I find myself obliged to believe that the mnemic quality in all living things (which is proved to exist by direct experiment) must depend on the physical changes in protoplasm, and that it is therefore permissible to use these changes as a notation in which the phenomena of habit may be expressed.

Habit illustrated by Morphology.

We have hitherto been considering the mnemic quality of movements; but, as I have attempted to show, morphological changes are reactions to stimulation of the same kind as these temporary changes. It is indeed from the morphological reactions of living things that the most striking cases of habit are, in my opinion, to be found.

The development of the individual from the germ-cell takes place by a series of stages of cell-division and growth, each stage apparently serving as a stimulus to the next, each unit following its predecessor like the movements linked together in an habitual action performed by an animal.

My view is that the rhythm of ontogeny is actually and literally a habit. It undoubtedly has the feature which I have described as pre-eminently characteristic of habit, viz., an automatic quality which is seen in the performance of a series of actions in the absence of the complete series of stimuli to which they (the stages of ontogeny) were originally due. This is the chief point on which I wish to insist—I mean that the resemblance between ontogeny and habit is not merely superficial, but deeply seated. It was with this conclusion in view that I dwelt, at the risk of being tedious, on the fact that memory has its place in the morphological as well as in the temporary reactions of living things. It cannot be denied that the ontogenetic rhythm has the two qualities observable in habit—namely, a certain degree of fixity or automaticity, and also a certain variability. A habit is not irrevocably fixed, but may be altered in various ways. Parts of it may be forgotten or new links may be added to it. In ontogeny the fixity is especially observable in the earlier, the variability in the later, stages. Mr. Darwin has pointed out that "on the view that species are only strongly marked and fixed varieties, we might expect often to find them still continuing to vary in those parts of their structure which have varied within a moderately recent period." These remarks are in explanation of the "notorious" fact that specific are more variable than generic character—a fact for which it is "almost superfluous to adduce evidence" ("Origin of Species," 6th edit., p. 122). This, again, is what we find in habit: take the case of a man who, from his youth up, has daily repeated a certain form of words. If in middle life an addition is made to the formula, he will find the recently acquired part more liable to vary than the rest.

Again, there is the wonderful fact that, as the ovum develops into the perfect organism, it passes through a series of changes which are believed to represent the successive forms through which its ancestors passed in the process of evolution. This is precisely paralleled by our own experience of memory, for it often happens that we cannot reproduce the last learned verse of a poem without repeating the earlier part; each verse is suggested by the previous one and acts as a stimulus for the next. The blurred and imperfect character of the ontogenetic version of the phylogenetic series may at least remind us of the tendency to abbreviate by omission what we have learned by heart.

In all bi-sexual organisms the ontogenetic rhythm of the offspring is a combination of the rhythms of its parents. This may or may not be visible in the offspring; thus in the crossing of two varieties the mongrel assumes the character of the prepotent parent. Or the offspring may show a blend of both parental characters. Semon "Die Mneme," 2nd Ed., pp. 147, 221, 303, 345) uses as a model the two versions of Goethe's poem:—

"Ueber allen Gipfeln, ist Ruh, in allen { Wäldern, hörest du, keinen Hauch. / Wipfeln, spürest du, kaum einen Hauch."

One of these terminations will generally be prepotent, probably the one that was heard first or heard most often. But the cause of such prepotency may be as obscure as the corresponding occurrence in the formation of mongrels. We can only say that in some persons the word "allen" releases the word "Wäldern," while in others, it leads up to "Wipfeln." Again, a mixture of the terminations may occur leading to such a mongrel form as: "in allen Wäldern hörest du kaum einen Hauch." The same thing is true of music; a man with an imperfect memory easily interpolates in a melody a bar that belongs elsewhere. In the case of memory the introduction of a link from one mental rhythm into another can only occur when the two series are closely similar, and this may remind us of the difficulty of making a cross between distinctly related forms.

Enough has been said to show that there is a resemblance between the two rhythms of development and of memory; and that there is at least a *prima facie* case for believing them to be essentially similar. It will be seen that my view is the same as that of Hering, which is generally described as the identification of memory and inheritance.* Hering says that "between the *me* of to-day and the *me* of yesterday lie night and sleep, abysses of unconsciousness; nor is there any bridge but memory with which to span them." And in the same way he claims that the abyss between two generations is bridged by the unconscious memory that resides in the germ cells. It is also the same as that of Semon, and to a great extent as that of Rignano ("Sur la Transmissibilité des Caractères Acquis," Paris, 1906). I, however, prefer at the moment to limit myself to asserting the identity of ontogeny and habit, or, more generally, to the assertion in Semon's phraseology, that ontogeny is a mnemic phenomenon.

Evolution, in its modern sense, depends on a change in the ontogenetic rhythm. This is obvious, since if this rhythm is absolutely fixed, a species can never give rise to varieties. This being so, we have to ask *in what ways* the ontogenetic rhythm can be altered. An habitual action, for instance, a trick learned by a dog, may be altered by adding new accomplishments; at first the animal will persist in finishing his performance at the old place, but at last the extended trick will be bonded into a rhythm of actions as fixed as was the original simpler performance. May we not believe that this is what has occurred in evolution.

We know from experiment that a plant may be altered in form by causes acting on it during the progress of development. Thus a beech tree may be made to develop different forms of leaves by exposing it to sunshine or to shade. The ontogeny is different in the two cases, and what is of special interest is, that there exist shade-loving plants in which a structure similar to that of the shaded beech-leaf is apparently typical of the species, but on this point it is necessary to speak with caution. In the same way Goebel points out that in some orchids the assimilating roots take on a flattened form when exposed to sunlight, but in others this morphological change has become automatic, and occurs even in darkness (Goebel's "Organography of Plants," Part II., p. 285).

* Everyone who deals with this subject must take his stand on the foundation laid by Hering in his celebrated Address given at Vienna in 1870, and reprinted in No. 148 of Ostwald's "Exakt Klassiker." The passage quoted (p. 14) is from Samuel Butler's translation of Hering in "Unconscious Memory," 1880, p. 110. Butler had previously elaborated the view that "we are one person with our ancestors" in his entertaining book "Life and Habit," 1878, and this was written in ignorance of Hering's views.

Such cases suggest at least the possibility of varieties arising as changes in or additions to the later stages of ontogeny. This is, briefly given, the epigenetic point of view.

But there is another way of looking at the matter—namely, that upheld by Galton and Weismann. According to this view ontogeny can only be changed by a fundamental upset of the whole system—namely, by an alteration occurring in its first stage, the germ cell, and this view is now very generally accepted.

The same type of change may conceivably occur in memory or habit; that is, the rhythm as a whole may be altered by some cause acting on the nerve-centres connected with the earlier links of the series. The analogy is not exact, but such an imaginary case is at least of a different type from a change in habit consisting in the addition of a new link or the alteration of one of the latest formed links. If we were as ignorant of the growth of human actions as we are of variation, we might have a school of naturalists asserting that all changes in habit originate in the earliest link of the series. But we know that this is not the case. On the other hand, I fully admit that the structure of an ovum may in this way be altered, and give rise to a variation which may be the starting-point of a new species.

But how can a new species originate according to an epigenetic theory? How can a change in the latter stages of ontogeny produce a permanent alteration in the germ-cells? Our answer to this question will depend on our views of the structure of the germ-cells. According to the mnemic theory they have the quality which is found in the highest perfection in nerve-cells, but is at the same time a character of all living matter—namely, the power of retaining the residual effects of former stimuli and of giving forth or reproducing under certain conditions an echo of the original stimulus. In Semon's phraseology germ-cells must, like nerve-cells, contain engrams, and these engrams must be (like nerve-engrams) bonded together by association, so that they come into action one after another in a certain order automatically, *i.e.*, in the absence of the original stimuli.

This seems to me the strength of the mnemic theory—namely, that it accounts for the preformed character of germ-cells by the building up in them of an organised series of engrams. But if this view has its strength, it has also its weakness. Routine can only be built up by repetition, but each stage in ontogeny occurs only once in a lifetime. Therefore if ontogeny is a routine each generation must be mnemically connected with the next. This can only be possible if the germ-cells are, as it were, in telegraphic communication with the whole body of the organism; so that as ontogeny is changed by the addition of new characters, new engrams are added to the germ-cell.

Thus, in fact, the mnemic theory of development depends on the possibility of what is known as somatic inheritance or the inheritance of acquired characters. This is obvious to all those familiar with the subject, but to others it may not be so clear. Somatic inheritance is popularly interesting in relation to the possible inherited effects of education, or of mutilations, or of the effects of use and disuse. It is forgotten that it may be, as I have tried to show, an integral part of all evolutionary development.

Weismann's Theory.

Everyone must allow that if Weismann's theory of inheritance is accepted we cannot admit the possibility of somatic inheritance. This may be made clear to those unfamiliar with the subject by an illustration taken from the economy of an ant's nest or beehive. The queen* on whom depends the future of the race is cut off from all active experience of life: she is a mere reproducing machine, housed, fed, and protected by the workers. But these, on whom falls the burden of the struggle for life and the experience of the world generally, are sterile, and take no direct share in the reproduction of the species. The queen represents Weismann's germ-plasm, the workers are the body or soma. Now imagine the colony exposed to some injurious change in environment; the salvation of the species will depend on whether or no an improved pattern of worker can be produced. This depends on the occurrence of appropriate variations, so that the queen bee and the drones, on whom this depends, are of central importance. On the other hand, any change occurring in the workers, for instance, increased skill due to practice in doing their work or changes in their structure due to external conditions, cannot possibly be inherited, since workers are absolutely cut off from the reproduction of the race. According to Weismann, there is precisely the same bar to the inheritance of somatic change.

The racial or phyletic life of all organisms is conceived by him as a series of germ-cells whose activity is limited to varying, and whose survival in any generation depends on the production of a successful soma or body capable of housing, protecting, and feeding the germ-cell. Most people would *à priori* declare that a community where experience and action are separated must fail. But the bee's nest, which must be allowed to be something more than an illustration of Weismann's theory, proves the contrary.

It is clear that there must be war to the knife between the theory of Weismann and that of the somatists—to coin a name for those who believe in the inheritance of acquired characters. A few illustrations may be given of the strength of Weismann's position. Some trick or trivial habit appears in two successive generations, and the son is said to inherit it from his father. But this is not necessarily a case of somatic inheritance, since, according to Weismann, the germ-plasm of both father and son contained the potentiality of the habit in question. If we keep constantly in view Weismann's theory of continuity, the facts which are supposed to prove somatic inheritance cease to be decisive.

Weismann has also shown by means of his hypothesis of "simultaneous stimulation"* the unconvincingness of a certain type of experiment. Thus Fischer showed that when chrysalids of *Arctia caja* are subjected to low temperature a certain number of them produce dark coloured insects; and further that these moths mated together yield dark coloured offspring. This has been held to prove somatic inheritance, but Weismann points out that it is explicable by the low temperature having an identical effect on the colour-determinants existing in the wing-rudiments of the pupa, and on the same determinants occurring in the germ-cells.

It does not seem to me worth while to go in detail into the evidence by which somatists strive to prove their point, because I do not know of any facts which are really decisive. That is to say, that though they are explicable as due to somatic inheritance, they never seem to me absolutely inexplicable on Weismann's hypothesis. But, as already pointed out, it is not necessary to look for special facts and experiments, since if the mnemic theory of ontogeny is accepted the development of every organism in the world depends on somatic inheritance.

I fully acknowledge the strength of Weismann's position; I acknowledge also most fully that it requires a stronger man than myself to meet that trained and well-tried fighter. Nevertheless, I shall venture on a few remarks. It must be rembered that, as Romanes pointed out ("An Examination of Weismann," 1893, pp. 169, 170), Weismann has greatly strengthened his theory of heredity by giving up the absolute stability and perpetual continuity of germ-plasm. Germ-plasm is no longer that mysterious entity, immortal and self-contained, which used to suggest a physical soul. It is no longer the aristocrat it was when its only activity was dependent on its protozoan ancestors,

* Nor do the drones share the activity of the workers.

* I borrow this convenient expression from Plate's excellent book, "Ueber die Bedeutung des Darwin'schen Selectionsprincips," 1903, p. 81.

when it reigned absolutely aloof from its contemporary subjects. The germ-plasm theory of to-day is liberalised, though it is not so democratic as its brother sovereign Pangenesis, who reigns, or used to reign, by an elaborate system of proportional representation. But in spite of the skill and energy devoted to its improvement by its distinguished author, Weismannism fails, in my opinion, to be a satisfactory theory of evolution.

All such theories must account for two things which are parts of a single process but may logically be considered separately:—(i.) The fact of ontogeny, namely, that the ovum has the capacity of developing into a certain more or less predetermined form; (ii.) the fact of heredity—the circumstance that this form is approximately the same as that of the parent.

The doctrine of pangenesis accounts for heredity, since the germ-cells are imagined as made up of gemmules representing all parts of the adult; but it does not account for ontogeny, because there seems to me no sufficient reason why the gemmules should become active in a predetermined order unless, indeed, we allow that they do so by habit, and then the doctrine of pangenesis become a variant of the mnemic theory.

The strength of Weismann's theory lies in its explanation of heredity. According to the doctrine of continuity, a fragment of the germ-plasm is, as it were, put on one side and saved up to make the germ-cell of the new generation, so that the germ-cells of two successive generations are made of the same material. This, again, depends on Weismann's belief that when the ovum divides, the two daughter cells are not identical; that, in fact, the fundamental difference between soma and germ-cells begins at this point. But this is precisely where many naturalists whose observations are worthy of all respect differ from him. Weismann's theory is therefore threatened at the very foundation.

Even if we allow Weismann's method of providing for the identity between the germ-cell of two successive generations, there remains, as above indicated, a greater problem namely, that of ontogeny. We no longer look at the potentiality of a germ-cell as Caliban looked on Setebos, as something essentially incomprehensible ruling the future in an unknown way—"just choosing so." If the modern germ-cell is to have a poetic analogue it must be compared to a Pandora's box of architectonic sprites which are let loose in definite order, each serving as a master-builder for a prescribed stage of ontogeny. Weismann's view of the mechanism by which his determinants—the architectonic sprites—come into action in due order is, I assume, satisfactory to many, but I confess that I find it difficult to grasp. The orderly distribution of determinants depends primarily on their arrangement in the ids, where they are held together by "vital affinities." They are guided to the cells on which they are to act by differential divisions, in each of which the determinants are sorted into two unequal lots. They then become active, *i.e.*, break up into biophores, partly under the influence of liberating stimuli and partly by an automatic process. Finally, the biophores communicate a "definite vital force" to the appropriate cells ("The Evolution of Theory," Eng. trans., i., 373 *et seq.*). This *may* be a description of what happens; but inasmuch as it fails to connect the process of ontogeny with physiological processes of which we have definite knowledge, it does not to me seem a convincing explanation.

For myself I can only say that I am not satisfied with Weismann's theory of heredity or of ontogeny. As regards the first, I incline to deny the distinction between germ and soma, to insist on the plain facts that the soma is continuous with the germ-cell, and that the somatic cells may have the same reproductive qualities as the germ-cells (as is proved by the facts of regeneration); that, in fact, the germ-cell is merely a specialised somatic cell and has the essential qualities of the soma. With regard to ontogeny, I have already pointed out that Weismann does not seem to explain its automatic character.

The Mnemic Theory.

If the mnemic theory is compared with Weismann's views it is clear that it is strong precisely where these are weakest—namely, in giving a coherent theory of the rhythm of development. It also bears comparison with all theories in which the conception of determinants occurs. Why should we make elaborate theories of hypothetical determinants to account for the potentialities lying hidden in the germ-cell, and neglect the only determinants of whose existence we have positive knowledge (though we do not know their precise nature)? We know positively that by making a dog sit up and then giving him a biscuit we build up something in his brain in consequence of which a biscuit becomes the stimulus to the act of sitting. The mnemic theory assumes that the determinants of morphological change are of the same type as the structural alteration wrought in the dog's brain.

The mnemic theory—at any rate that form of it held by Semon and by myself—agrees with the current view, viz., that the nucleus is the centre of development, or, in Semon's phraseology, that the nucleus contains the engrams in which lies the secret of the ontogenetic rhythm. But the mode of action of the mnemic nucleus is completely different from that of Weismann. He assumes that the nucleus is disintegrated in the course of development by the dropping from it of the determinants which regulate the manner of growth of successive groups of cells. But if the potentiality of the germ nucleus depends on the presence of engrams, if, in fact, its function is comparable to that of a nerve-centre, its capacity is not diminished by action; it does not cast out engrams from its substance as Weismann's nucleus is assumed to drop armies of determinants. The engrams are but cut deeper into the records, and more closely bonded one with the next. The nucleus, considered as a machine, does not lose its component parts in the course of use. We shall see, later on, that the nuclei of the whole body may, on the mnemic theory, be believed to become alike. The fact that the mnemic theory allows the nucleus to retain its repeating or reproductive or mnemic quality supplies the element of continuity. The germ-cell divides and its daughter cells form the tissues of the embryo, and in this process the original nucleus has given rise to a group of nuclei; these, however, have not lost their engrams, but retain the potentiality of the parent nucleus. We need not therefore postulate the special form of continuity which is characteristic of Weismann's theory.

We may say therefore that the mnemic hypothesis harmonises with the facts of heredity and ontogeny. But the real difficulties remain to be considered, and these, I confess, are of a terrifying magnitude.

The first difficulty is the question how the changes arising in the soma are, so to speak, telegraphed to the germ-cells. Hering allows that such communication must at first seem highly mysterious.* He then proceeds to show how by the essential unity and yet extreme ramification of the nervous system "all parts of the body are so connected that what happens in one echoes through the rest, so that from the disturbance occurring in any part some notification, faint though it may be, is conveyed to the most distant parts of the body."

A similar explanation is given by Nägeli. He supposes that adaptive, in contradistinction to organic, characters are produced by external causes; and since these characters are hereditary there must be communication between the seat of adaptation and the germ-cells. This telegraphic effect is supposed to be effected by the network of idioplasm which traverses the body, in the case of plants by the intercellular protoplasmic threads.

Semon faces the difficulty boldly. When a new character appears in the body of an organism, in response to changing environment, Semon assumes that a new

* E. Hering in Ostwald's "Klassiker der exakten Wissenschaften," No. 148, p. 14; see also S. Butler's translation in "Unconscious Memory," p. 119.

engram is added to the nuclei in the part affected; and that, further, the disturbance tends to spread to all the nuclei of the body (including those of the germ-cells), and to produce in them the same change. In plants the flow must be conceived as travelling by intercellular plasmic threads, but in animals primarily by nerve-trunks. Thus the reproductive elements must be considered as having in some degree the character of nerve-cells. So that, for instance, if we are to believe that an individual habit may be inherited and appear as an instinct, the repetition of the habit will not merely mean changes in the central nervous system, but also corresponding changes in the germ-cells. These will be, according to Semon, excessively faint in comparison to the nerve-engrams, and can only be made efficient by prolonged action. Semon lays great stress on the slowness of the process of building up efficient engrams in the germ-cells.

Weismann* speaks of the impossibility of germinal engrams being formed in this way. He objects that nerve-currents can only differ from each other in intensity, and therefore there can be no communication of potentialities to the germ-cell. He holds it to be impossible that somatic changes should be telegraphed to the germ-cell and be reproduced ontogenetically—a process which he compares to a telegram despatched in German and arriving in Chinese. According to Semon,† what radiates from the point of stimulation in the soma is the primary excitation set up in the somatic cells; if this is so, the radiating influence will produce the same effect on all the nuclei of the organism. My own point of view is the following:—In a plant (as already pointed out) the ectoplasm may be compared to the sense-organ of the cell, and the primary excitation of the cell will be a change in the ectoplasm; but since cells are connected by ectoplasmic threads the primary excitation will spread and produce in other cells a faint copy of the engram impressed on the somatic cells originally stimulated. But in all these assumptions we are met by the question to which Weismann has called attention—namely, whether nervous impulses can differ from one another in *quality*?‡ The general opinion of physiologists is undoubtedly to the opposite effect—namely, that all nervous impulses are identical in quality. But there are notable exceptions; for instance, Hering ("Zur Theorie der Nerventhätigkeit, Akademische Vortrag," 1898, Veit, Leipzig), who strongly supports what may be called the qualitative theory. I am not competent to form an opinion on the subject, but I confess to being impressed by Hering's argument that the nerve cell and nerve fibre, as parts of one individual (the neuron), must have a common irritability. On the other hand, there is striking evidence, in Langley's experiments on the cross-grafting of efferent nerves, that here at least nerve impulses are interchangeable and therefore identical in quality (*Proc. Roy. Soc.*, 1904, p. 99; *Journal of Physiology*, xxiii., p. 240, and xxxi., p. 365). The state of knowledge as regards afferent nerves is, however, more favourable to my point of view. For the difficulties that meet the physiologist—especially as regards the nerves of smell and hearing—are so great that it has been found simpler to assume differences in impulse-quality rather than attempt an explanation of the facts on the other hypothesis (see Nagel, "Handbuch der Physiologie des Menschen," 1905, iii., pp. 1—15).

On the whole it may be said that, although the trend of physiological opinion is against the general existence of qualitative difference in nerve-impulses, yet the question cannot be said to be settled either one way or the other.

Another obvious difficulty is to imagine how within a single cell the engrams or potentialities of a number of actions can be locked up. We can only answer that the nucleus is admittedly very complex in structure. It may be added (but this not an answer) that in this respect it claims no more than its neighbours; it need not be more complex than Weismann's germ-plasm. One conceivable simplification seems to be in the direction of the pangenes of De Vries. He imagines that these heritage-units are relatively small in number, and that they produce complex results by combination, not by each being responsible for a minute fraction of the total result (De Vries, "Intracellular Pangenesis," p. 7). They may be compared to the letters of the alphabet which by combination make an infinity of words.* Nägeli (Nägeli's "Abstammungslehre, 1884, p. 73) held a similar view. "To understand heredity," he wrote, "we do not need a special independent symbol for every difference conditioned by space, time, or quality, but a substance which can represent every possible combination of differences by the fitting together of a limited number of elements, and which can be transformed by permutations into other combinations." He applied (*loc. cit.*, p. 59) the idea of a combination of symbols to the telegraphic quality of his idioplasm. He suggests that as the nerves convey the most varied perceptions of external objects to the central nervous system, and there create a coherent picture, so it is not impossible that the idioplasm may convey a combination of its local alterations to other parts of the organism.

Another theory of simplified telegraphy between soma and germ-cell is given by Rignano.† I regret that the space at my command does not permit me to give a full account of his interesting speculation on somatic inheritance. It resembles the theories of Hering, Butler, and Semon in postulating a quality of living things, which is the basis both of memory and inheritance. But it differs from them in seeking for a physical explanation or model of what is common to the two. He compares the nucleus to an electric accumulator which in its discharge gives out the same sort of energy that it has received. How far this is an allowable parallel I am not prepared to say, and in what follows I have given Rignano's results in biological terms. What interests me is the conclusion that the impulse conveyed to the nucleus of the germ-cell is, as far as results are concerned, the external stimulus. Thus, if a somatic cell (A) is induced by an external stimulus (S) acting on the nucleus to assume a new manner of development, a disturbance spreads through the organism, so that finally the nuclei of the germ-cells are altered in a similar manner. When the cellular descendants of the germ-cells reach the same stage of ontogeny as that in which the original stimulation occurred, a stimulus comes into action equivalent to S as regards the results it is capable of producing. So that the change originally wrought in cell A by the actual stimulus S is now reproduced by what may be called an inherited stimulus. But when A was originally affected other cells, B, C, D, may have reacted to S by various forms of growth. And therefore when during the development of the altered germ-cell something equivalent to S comes into play, there will be induced, not merely the original change in the development of A, but also the changes which were originally induced in the growth of B, C, D. Thus, according to Rignano, the germ-nucleus releases a number of developmental processes, each of which would, according to Weismann, require a separate determinant.

If the view here given is accepted, we must take a new view of Weismann's cases of *simultaneous stimulation*, *i.e.*, cases like Fischer's experiments on *Arctia caja*, which he does not allow to be somatic inheritance. If we are right in saying that, the original excitation of the soma is transferred to the germ-cell, and it does not matter whether the stimulus is transferred by "telegraphy," or whether a given cause, *e.g.*, a low temperature, acts simultaneously

* Weismann, "The Evolution Theory," 1904, vol. ii., p. 63; also his "Richard Semon's 'Mneme' und die Vererbung erworbener Eigenschaften," in the *Archiv für Rassen- und Gesellschafts-Biologie*, 1906. Semon has replied in the same journal for 1907.

† Semon ("Mneme," ed. i., p. 142), does not, however, consider it proved that the nucleus is necessarily the smallest element in which the whole inheritance resides. He refers especially to the regeneration of sections of *Stentor* which contain mere fragments of the nucleus.

‡ I use this word in the ordinary sense without reference to what is known as *modality*.

* I take this comparison from Lotsy's account of De Vries' theory. Lotsy, "Vorlesungen über Deszendenztheorien," 1906, i., p. 98.

† For what is here given I am partly indebted to Signor Rignano's letters.

on soma and germ-cell. In both cases we have a given alteration produced in the nuclei of the soma and the germ-cell. Nägeli used the word *telegraphy* to mean a dynamic form of transference, but he did not exclude the possibility of the same effect being produced by the movement of chemical substances, and went so far as to suggest that the sieve tubes might convey such stimuli in plants. In any case this point of view deserves careful consideration (see Semon, *Archiv. f. Rassen- und Gesellschafts-Biologie*, 1907, p. 39).

Still another code of communication seems to me to be at least conceivable. One of the most obvious characteristics of animal life is the guidance of the organism by certain groups of stimuli, producing either a movement of seeking—positive reaction (see Jennings, "Behaviour of the Lower Organisms")—or one of avoidance—negative reaction. Taking the latter as being the simplest, we find that in the lowest as in the highest organisms a given reaction follows each one of a number of diverse conditions which have nothing in common save that they are broadly harmful in character. We withdraw our hands from a heated body, a prick, a corrosive substance, or an electric shock. The interesting point is that it is left to the organism to discover by the method of trial and error the best means of dealing with a subinjurious stimulus. May we not therefore say that the existence of pleasure and pain simplifies inheritance? It certainly renders unnecessary a great deal of detailed inheritance. The innumerable appropriate movements performed by animals are broadly the same as those of their parents, but they are not necessarily inherited in every detail; they are rather the unavoidable outcome of hereditary but unspecialised sensitiveness. It is as though heredity were arranged on a code-system instead of by separate signals for every movement of the organism.

It may be said that in individual life the penalty of failure is pain, but that the penalty for failure in ontogenetic morphology is death. But it is only because pain is the shadow cast by Death as he approaches that it is of value to the organism. Death would be still the penalty of creatures that had not acquired this sensitiveness to the edge of danger. Is it not possible that the sensitiveness to external agencies by which structural ontogeny is undoubtedly guided may have a similar quality, and that morphological variations may also be reactions to the edge of danger. But this is a point of view I cannot now enter upon.

It may be objected that the inheritance of anything so complex as an instinct is difficult to conceive on the mnemic theory. Yet it is impossible to avoid suspecting that at least some instincts originate in individual acquirements, since they are continuous with habits gained in the lifetime of the organism. Thus the tendency to peck at any small object is undoubtedly inherited; the power of distinguishing suitable from unsuitable objects is gained by experience. It may be said that the engrams concerned in the pecking instinct cannot conceivably be transferred from the central nervous system to the nucleus of the germ-cells. To this I might answer that this is not more inconceivable than Weismann's assumption that the germ-cell chances to be so altered that the young chicken pecks instinctively. Let us consider another case of what appears to be an hereditary movement. Take, for instance, the case of a young dog, who in fighting bites his own lips. The pain thus produced will induce him to tuck up his lips out of harm's way. This protective movement will become firmly associated with, not only the act of fighting but with the remembrance of it, and will show itself in the familiar snarl of the angry dog. This movement is now, I presume, hereditary in dogs, and is so strongly inherited by ourselves (from simiam ancestors) that a lifting of the corner of the upper lip is a recognised signal of adverse feeling. Is it really conceivable that the original snarl is due to that unspecialised stimulus we call pain, whereas the inherited snarl is due to fortuitous upsets of the determinants in the germ cell?

I am well aware that many other objections may be advanced against the views I advocate. To take a single instance, there are many cases where we should expect somatic inheritance, but where we look in vain for it. This difficulty, and others equally important, must for the present be passed over. Nor shall I say anything more as to the possible means of communication between the soma and the germ-cells. To me it seems conceivable that some such telegraphy is possible. But I shall hardly wonder if a majority of my hearers decide that the available evidence in its favour is both weak and fantastic. Nor can I wonder that, apart from the problem of mechanism, the existence of somatic inheritance is denied for want of evidence. But I must once more insist that according to the mnemic hypothesis, somatic inheritance lies at the root of all evolution. Life is a gigantic experiment which the opposing schools interpret in opposite ways. I hope that in this dispute both sides will seek out and welcome decisive results. My own conviction in favour of somatic inheritance rests primarily on the automatic element in ontogeny. It seems to me certain that in development we have an actual instance of habit. If this is so, somatic inheritance must be a *vera causa*. Nor does it seem impossible that memory should rule the plasmic link which connects successive generations—the true miracle of the camel passing through the eye of a needle—since, as I have tried to show, the reactions of living things to their surroundings exhibit in the plainest way the universal presence of a mnemic factor.

We may fix our eyes on phylogeny and regard the living world as a great chain of forms, each of which has learned something of which its predecessors were ignorant; or we may attend rather to ontogeny, where the lessons learned become in part automatic. But we must remember that the distinction between phylogeny and ontogeny is an artificial one, and that routine and aquisition are blended in life.*

The great engine of natural selection is taunted nowadays, as it was fifty years ago, with being merely a negative power. I venture to think that the mnemic hypothesis of evolution makes the positive value of natural selection more obvious. If evolution is a process of drilling organisms into habits, the elimination of those that cannot learn is an integral part of the process, and is no less real because it is carried out by a self-acting system. It is surely a positive gain to the harmony of the universe that the discordant strings should break. But natural selection does more than this; and just as a trainer insists on his performing dogs accommodating themselves to conditions of increasing complexity, so does natural selection pass on its pupils from one set of conditions to other and more elaborate tests, insisting that they shall endlessly repeat what they have learned and forcing them to learn something new. Natural selection attains in a blind, mechanical way the ends gained by a human breeder; and by an extension of the same metaphor it may be said to have the power of a trainer—of an automatic master with endless patience and all time at his disposal.

New Crystallised Sugar, Perseulose, with Seven Carbon Atoms.—Gabriel Bertrand.—The oxidation of perseite by means of the bacteria of sorbose yields a new crystalline sugar to which the author has given the name perseulose. It resembles glucose in appearance, and its formula is $C_7H_{14}O_7$. It is lævorotatory, and, like other reducing sugars, possesses the property of multirotation. Its reducing power is inferior to that of glucose but greater than that of sorbose. It yields a crystalline osazone, $C_{19}H_{24}N_4O_5$. Perseulose is the first reducing sugar with seven atoms of carbon produced by a living cell, which has been isolated.—*Comptes Rendus*, cxlvii., No. 3.

* This subject is dealt with in a very interesting manner in Professor James Ward's forthcoming lectures on the "Realm of Ends." Also in his article on "Mechanism and Morals," in the *Hibbert Journal*, October, 1905, p. 92; and in his article on Psychology in the "Encyclopædia Britannica," 1886, xx., p. 44.

THE ELECTROLYTIC PROPERTIES OF DILUTE SOLUTIONS OF SULPHURIC ACID.*

By W. C. D. WHETHAM, M.A. F.R.S., and H. H. PAINE, B.A., Trinity College, Cambridge.

(Continued from p. 100).

PART II.—*By* H. H. PAINE.

1. *Method of Experiment.*

THE migration constant was determined for solutions of sulphuric acid of concentration varying from 0·1 to 0·00005 normal. A current, the strength of which was determined by means of a standardised galvanometer, was passed through the migration cell, and the total change in the quantity of solute round the anode and cathode measured. As explained in the first part of this paper, the value of this change in gramme-equivalents, divided by the number of gramme-equivalents of hydrogen evolved at the cathode, gives us the migration constant for the solution.

The great advantage of sulphuric acid for these experiments is that no uncertain reactions take place at either anode or cathode. Measurements of the change in concentration at the two electrodes are thus equally trustworthy, and each serves as a check on the other.

The solutions used were made up with water having a specific conductivity of from $0{\cdot}9\times10^{-6}$ to $1{\cdot}0\times10^{-6}$ reciprocal ohm at 18° C. Ordinary distilled water was redistilled in a Jena glass apparatus with a trace of sulphuric acid and of potassium bichromate. A stock solution of sulphuric acid (of strength about 0·1 normal) was prepared from some pure 50 per cent sulphuric acid supplied by Messrs. Baird and Tatlock. The conductivity of this solution was measured, and its exact strength thence determined by means of Kohlrausch's tables. Dilute solutions were obtained from this by taking a weighed quantity and adding the requisite amount of water.

After the passage of the current through the migration cell, the strengths of the solutions in the anode and cathode regions were determined by measuring their conductivities. For this purpose it is necessary to know how the conductivity varies with concentration. The relation between the two has been determined by several observers, and the results plotted in the form of a curve showing the ratio of the equivalent conductivity to the cube root of the concentration. It was thought advisable, however, to have such a curve for the actual solution under observation. Since the solutions were all made up gravimetrically from the original one, we have at once a means of finding the concentration (in terms of that of the original). The conductivity was also measured. Each solution made up thus gave a point on the curve. From the curve so drawn, calculations were made for determining the strengths of the two solutions after the passage of the current. Slight effects due to the solution of impurities during the course of the experiment would give too small a value for the change in concentration on the one side, and too large a value on the other; taking the mean therefore tends to eliminate these effects; agreement between the changes on the two sides is a sure test that such errors have not entered to vitiate the results. This is a very important consideration, for with such weak solutions as were used, fouling, not only by the solution of solid matter from the surface of the vessel, but also by the absorption of gases such as ammonia from the air, is very likely to occur. Without such a check it would be dangerous to draw any conclusions as to the value of the migration constant for solutions weaker than 0·0001 normal, whereas, with the help of this check, successful experiments were conducted with solutions as weak as 0·00005 normal.

2. *Apparatus.*

1. *Conductivity Cells.*—Two cells were used in the course of the experiments for the purpose of measuring the conductivity, one for the two strongest solutions (0·1 and 0·01 N), and the other for solutions of strength 0·001 N and under.

The electrodes in both cells were of platinum, but in the case of the cell used for the stronger solutions (Fig. 2), they were coated with platinum-black, while in the other cell (Fig. 3), after platinisation, they had been heated to redness before being sealed into the glass. In the second cell, contact with the electrodes was made by means of mercury poured into the side tubes. The centre tube leading to the cell-chamber was closed with a glass cap, by the use of which, it was found, fouling from the atmosphere was prevented completely.

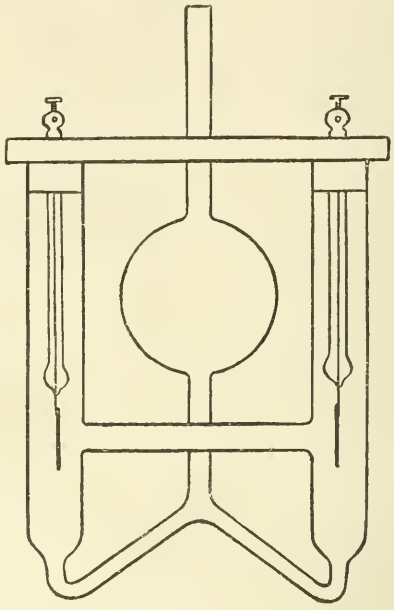

FIG. 2.

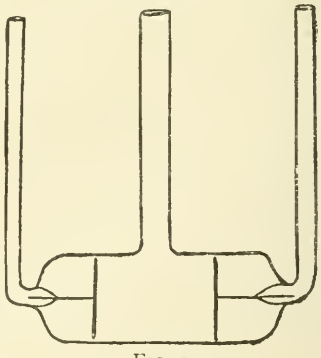

FIG. 3.

The cell-constant for each cell was determined by means of a standard potassium chloride solution made up from the carefully prepared, pure, crystallised salt. Knowing the concentration of this solution, we can calculate its conductivity (in reciprocal ohms) from the tables compiled by Kohlrausch.

The resistance in each case was determined by the method of Wheatstone's bridge. By the use of the commutator described in a paper by one of the authors (*Phil. Trans.*, 1900, A, cclix., 321), an alternating current was obtained, and at the same time a galvanometer used for testing the balance. The commutator was driven at the requisite speed by means of a small electric motor. In all

* A Paper read before the Royal Society, June 18, 1908.

measurements of the resistance the cell was placed in a bath of water kept well stirred and maintained at a temperature of 18° C., as shown by a Beckmann thermometer reading to hundredths of a degree. The temperature of the solution was regarded as constant and uniform when the measured resistance remained unaltered with time.

2. *The Migration Cell.*—This has been described in the first part of the paper. It may further be noticed here that by placing a pair of electrodes on each side, it was possible to measure the resistances of both portions of the liquid immediately before and immediately after the passage of the current, without transference to other conductivity cells. An almost certain cause of fouling was thus avoided. This device could be employed only for the weaker solutions (0·0002 N and under), as the resistances in the case of stronger solutions would be too small to be measured accurately with these electrodes. But with the stronger solutions, any possible fouling on transfer would be inappreciable.

3. *Galvanometer.*—The current through the migration cell was measured by means of a Nalder's moving-coil galvanometer, which, with the shunts used in the experiment, was previously standardised. This was done in the following way:—A current from a single storage cell (with a suitable resistance in series) was passed through a milliampère- (or volt-) meter, of resistance exactly 1 ohm. The terminals of the galvanometer were connected with the terminals of the ampère-meter through convenient resistances. From the reading of the ampère-meter and a knowledge of the resistance in the galvanometer circuit, we can calculate the current through the galvanometer. The deflections of the suspended coil of the galvanometer (observed by the ordinary reflection method) were noted simultaneously.

3. *Experimental Details.*

The method of procedure for solutions of strengths 0·0005 normal and over, differed slightly from that for weaker solutions. In the case of the stronger solutions the conductivity was too great for the resistance to be measured by means of the electrodes in the migration cell. Hence, the liquid had to be transferred to a conductivity cell. The conductivity of the original solution was first determined in one of these cells, in order to obtain a point on the equivalent conductivity curve. Some of the solution was then poured into the migration cell until the connecting tube was completely filled. The current (supplied by a hundred small storage cells) was passed through the apparatus for a time (generally ten to fifteen minutes) sufficient to produce on the average a 10 per cent change in the strength of the solutions; that is to say, until 10 per cent of the sulphate ions on the cathode side had migrated to the anode region. When the current had been stopped, the air pressure in the inverted V-tube was raised until the liquid had been forced to the ends of the tube, thus separating the anode and cathode portions. Each portion was then well stirred, and afterwards transferred by means of a syphon to a weighed flask, the syphon and flask having been carefully rinsed with pure water, and dried, before using. After the weight had been taken the solution was poured into the conductivity cell, and its resistance measured.

For solutions weaker than 0·0005 normal, the initial conductivity was determined in the conductivity cell as before. After the solution had been poured into the migration cell, the air pressure in the inverted V-tube was raised until the liquid had descended to the ends of the tube. The resistance on each side was measured, the solution being well stirred, and the temperature maintained at 18° C. After the air pressure had been released, and the liquid had risen to its former level, the current was passed through for the required time. The anode and cathode portions were again separated, as at the beginning of the experiment, and the resistances measured. Finally, the two portions were separately drawn off by means of a syphon, and weighed. The final conductivities are easily calculated, from the fact that they bear to the initial conductivity the ratios of the resistances (measured in the migration cell) at the beginning, to those at the end, of the experiment.

In calculating the conductivity of the sulphuric acid, the conductivity of the solvent was deducted from that of the solution in every case.

4. *Experimental Results.*

The following example shows the complete method of calculation for one of the experiments:—

Solution 20.

Original strength (as made up from a standard solution)	$1{\cdot}0140\times10^{-7}$ grm.-equiv. per cc. ($=m_0$)
Resistance in conductivity cell	12916 ohms
Cell constant	0·4532
Conductivity of solution ..	$\frac{0{\cdot}4532}{12916} = 3{\cdot}509\times10^{-5}$ recip. ohm
Conductivity of water (solvent)	$0{\cdot}103\times10^{-5}$ „
Conductivity of acid (solute)	$3{\cdot}406\times10^{-5}$ „ ($=k_0$)

(Hence $k_0/m_0 = 336{\cdot}0$, $\sqrt[3]{m_0} = 0{\cdot}0466$).

	Anode region.	Cathode region.
Resistances in migration cell, before	4825 ohms	5012 ohms
Resistances in migration cell, after	4276 „	5716 „
Weights of solutions ..	53·74 grms.	55·56 grms.

Calculations.

Anode side—

Conductivity after experiment	$3{\cdot}509\times10^{-5}\times\frac{4825}{4276} = 3{\cdot}959\times10^{-5}$ recip. ohm
Conductivity of water ..	$0{\cdot}103$
Conductivity of acid (solute)	$3{\cdot}856\times10^{-5}$ ($=k_a$)
Concentration from curve $\left(\frac{k_a}{(k/m)}\right)$	$\frac{3{\cdot}856\times10^{-5}}{339{\cdot}0} = 1{\cdot}1377\times10^{-7}$ grm. - equiv. per cc.
Increase in concentration	$0{\cdot}1237\times10^{-7}$
Total increase in quantity of acid	$0{\cdot}1237\times10^{-7}\times53{\cdot}74 = 0{\cdot}665\times10^{-6}$ grm. equiv.,

Cathode side—

Conductivity after experiment	$3{\cdot}509\times10^{-}\times\frac{5012}{5716} = 3{\cdot}077\times10^{-}$ recip. ohm
Conductivity of water ..	$0{\cdot}103$
Conductivity of acid (solute)	$2{\cdot}974\times10^{-5}$ „ ($=k_c$)
Concentration from curve $\left(\frac{k_c}{(k/m)}\right)$	$\frac{2{\cdot}974\times10^{-}}{332{\cdot}0} = 0{\cdot}8960\times10^{-7}$ grm. - equiv. per cc.
Decrease in concentration	$0{\cdot}1180\times10^{-7}$
Total increase in quantity of acid	$0{\cdot}1180\times10^{-7}\times55{\cdot}56 = 0{\cdot}655\times10^{-6}$ grm.-equiv.
Mean of change for two sides	$0{\cdot}660\times10^{-6}$ „
Current through cell ..	$4{\cdot}53\times10^{-1}$ ampère
Flowed for 12 mins. ..	= 720 secs.

Hence the number of grm.-equiv. of hydrogen liberated $= 4{\cdot}53 \times 10^{-4} \times 720 \times 1{\cdot}036 \times 10^{-5} = 3{\cdot}38 \times 10^{-6}$.

Migration constant or transport ratio .. $= \frac{0{\cdot}660 \times 10^{-6}}{3{\cdot}38 \times 10^{-6}} = 0{\cdot}195$.

(To be continued).

NOTICES OF BOOKS.

Chemie und Biologie der Pflanzlichen Sekrete. ("The Chemistry and Biology of the Secretions of Plants"). By A. Tschirch. Leipzig: Akademische Verlagsgesellschaft. 1908.

The author of this lecture, which was delivered before the Swiss Chemical Society, has made his name widely known by his researches on the application of the methods and principles of organic chemistry to biological problems, and the reprint gives a clear summary of our present knowledge of the secretions of plants. The word secretion is interpreted in its narrower sense, being taken to include resins and ethereal oils only, and of these the former are more particularly considered. The history of their investigation is discussed in an impartial and broad-minded spirit, and the doctrine of their formation without the collaboration of the plasma, in a special membrane layer, is put forward and explained. An interesting account is given of the author's own work on the isolation of some of the important resins, and the decomposition of them into their constituents, and the lecture concludes with a short discussion of the theory that the formation of plant secretions is due to the action of enzymes.

CORRESPONDENCE.

POTENTIAL ENERGY OF THE ELEMENTS.

To the Editor of the Chemical News.

Sir,—Since the publication of my paper on the "Potential Energy of the Elements" (Chemical News, xcvii., 302), my attention has been drawn to a recently published correction of a factor, based on more extended research that affects the values I have given for the potentials of the members of the helium family of elements. I have accordingly re-calculated them with this correction as follows:—

He	134487 K
Na	23338 ,,
Ca	13415 ,,
Sr	6141 ,,
Ba	2516 ,,

—I am, &c.,

Daniel J. Rankin.

August 21, 1908.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. cxlvii., No. 3, July 20, 1908.

Hydrates of Strontium and Barium Oxides.—M. de Forcrand.—In a vacuum at about +10° the hydrate, $SrO + 9H_2O$, is very slowly dehydrated. It yields $SrO + 2H_2O$ after a week, and this substance continues to lose water for a month, the final product being $SrO + H_2O$. To get the anhydrous oxide this must be heated in dry hydrogen to 850° for some time. These results are obtained much more quickly when $SrO + 9H_2O$ is heated to 45—50° in a current of dry hydrogen, although the temperature has to be raised to 850° to ensure complete dehydration. Between the monohydrate and the anhydrous oxide intermediate substances, *e.g.*, $SrO + 0{\cdot}22H_2O$, $SrO + 0{\cdot}06H_2O$, appear to be formed. With barium oxide the phenomena exhibited are similar, but there is no evidence of the existence of the intermediate substances. Thus it is more difficult to pass from $SrO + H_2O$ to SrO than from $BaO + H_2O$ to BaO. It seems probable that the formulæ of the anhydrous oxides are really $(SrO)_x$ and $(BaO)_x$, instead of SrO and BaO, and there is reason to believe that, in the case of oxides of polyvalent metals at any rate, the progressive condensations with partial dehydration are produced by a mechanism analogous to that of the formation of anhydrides and ethers or hydrates of carbon in organic chemistry.

Researches on the Ketodiacids.—E. E. Blaise and H. Gault.—The saponification of oxalsuccinic ether by hydrochloric acid in the cold, followed by boiling to eliminate the β-ketoacid function, yields α-ketoglutaric acid,—

$$CO_2C_2H_5{-}CO \atop CO_2C_2H_5{>}\overset{\alpha}{C}H{-}\overset{\alpha'}{C}H_2{-}CO_2C_2H_5 \rightarrow$$

$$\rightarrow CO_2H{-}\overset{\alpha}{C}O{-}\overset{\beta}{C}H_2{-}\overset{\alpha'}{C}H_2{-}CO_2H.$$

Excellent yields of α′-methyl-α-oxalsuccinic ether can be obtained by condensing ethyl pyrotartrate with ethyl oxalate by means of sodium ethylate. The condensation of dioxalsuccinic ether with concentrated hydrochloric acid at the ordinary temperature gives an acid compound, from which, by boiling, the author has prepared isopyromucic acid, which must be β-oxy-α-pyrone. The acid compound is therefore the α′-carboxyl derivative of β-oxy-α-pyrone.

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THE CHEMICAL NEWS.

Vol. XCVIII., No. 2546.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

Dublin, 1908.

By Prof. F. S. KIPPING, D.Sc., Ph.D., F.R.S., President of the Section.

On taking the Chair of this Section my first duty is to express my personal thanks to the Council of the British Association for having chosen me to fill the position of honour.

At this meeting the Association is enjoying, not for the first, but for the fourth time, the generous and genial hospitality of the citizens of Dublin; it is my privilege, on behalf of all the members of this Section, to tender our cordial thanks to our hosts for giving us this opportunity of meeting again in the capital of Ireland.

During the past few months we have read in the daily journals—and we sincerely hope it may be true—that there are signs of the commencement of a great development of the resources of this Island; as such a desirable event must be closely connected with, and, indeed, may even be dependent on, the vitality of the chemical industries of the country, the moment seems opportune for the consideration of a subject which has a direct bearing on both commerce and chemistry.

Although this Section is chiefly occupied with matters relating to pure science, the discussion of industrial questions is also regarded as one of its important functions; it does not attempt to distinguish pure from applied chemistry, and any problem which concerns either is deemed worthy of its attention.

From this point of view I propose to consider whether any steps can be taken to place the chemical industries of the United Kingdom of Great Britain and Ireland in a more prominent position than that which they now occupy in the world of commerce.

The subject is now new; it has been dealt with by many, but principally by those more directly interested—prominent members of the Society of Chemical Industry, who are far better qualified to express opinions on commercial matters than am I. It is perhaps presumption on my part to attempt to add anything to what has been said by such leaders of industrial chemistry, but I propose to deal with the subject from a very different standpoint—namely, from that of the teacher in the class-room and laboratory. Even if I fail to make a single suggestion of immediate practical value, the question is one of such magnitude and so many-sided that I feel justified in bringing it under the notice of this Section. It is not merely a matter of money, of a few millions or of a few tens of millions sterling. There are few branches of industry to which chemistry, in one way or another, is not of supreme importance. Whether we look to the great shipbuilding interests, dependent on the progress of metallurgy; to our cotton and linen trades, where cellulose reigns supreme; to our dye-houses or to our breweries, or to any other industry, great or small, there do we find problems in chemistry awaiting solution, and the nation which solves them will not only progress in civilisation and contentment, but will also justly claim to have taken a leading part in the advancement of science.

It is not then in any grudging spirit of envy that we approach this question; recognising the splendid work of men of other countries, rejoicing in the services which they have rendered to the world at large, our only desire is not to lag behind in the general intellectual and industrial advance of nations.

It is unnecessary to trouble you with any detailed comparison of the position which we occupy to-day with that which we have taken in the past. The fiftieth anniversary of the epoch-making discovery of mauve was held only two years ago, and the proceedings are still fresh in our recollection; the pæans of congratulation addressed to the discoverer (now, alas! no longer with us) were marred by a plaintive note, a note of lamentation over our lost industry, the manufacture of dyes. The jubilee of the founder of the colour industry in this country was also the occasion for pronouncing its funeral oration. If this were the full extent of our loss we might bear it with equanimity; but it is not so much what has already gone as what is going and what may go that are matters of such deep concern. Those who doubt the seriousness of our condition may find statistical evidence, more than sufficient to convince them, in the technical journals and in the Board of Trade reports of recent years.

The facts there disclosed show that in the manufacture of "fine chemicals," including perfumes, alkaloids, and crude coal-tar products, as well as dyes, the decadence of our industry is far advanced; in the case of heavy chemicals our position, perhaps, is not quite so serious at the present moment, but the future is dark and threatening. Chemical industries are so intimately connected and dependent on one another, that the fate of one may determine the fate of all; the by-product of one process is often the raw material of another. Who, then, can deny that the patience, perseverance, and high scientific skill, which have built up the colour industry abroad, if applied, as they have been and are being applied, to the manufacture of heavy chemicals, will not soon defy all competition from less progressive countries?

Such a possibility is full of national danger. It has been pointed out—and the prophecy cannot be regarded as unduly pessimistic—that from present indications a time will arrive when we shall be dependent on outside sources, not only for our food-supply, but also for our means of self-defence. When nitrates are exhausted, when nitric acid and ammonia are prepared from the components of the atmosphere, when all chemical industries have been so highly developed abroad that they have completely vanished from these Islands, and when their loss has reacted on all our other important industries, then, indeed, shall we feel the pinch of poverty; then, indeed, must we submit to national decay.

Is it possible to remedy the present unsatisfactory state of affairs, and to guard against an ominous future?

During the Perkin Jubilee celebrations Professor Carl Duisberg answered this question, in so far as it concerns the coal-tar colour industry, by an uncompromising negative. In an able and interesting speech he pointed out that, although the Briton is in general a practical man, he is lacking in patience, in the power of waiting for success; he expects to be compensated in hard cash, and at once, for his work or for his capital outlay. The German, on the other hand, is primarily a theorist possessing endless patience, and works without any immediate prospect of pecuniary reward; he has now learnt to be practical as well, but not at the expense of his ideals. It is to this happy combination of qualities that Professor Duisberg ascribes the success of his countrymen in the coal-tar colour industry—a success which he considers we are powerless to emulate, with which it would be futile for us to try and compete.

With this view that our chemical industries must submit to gradual extinction, even when it is held by so high an authority, we cannot and must not agree; if one nation can learn to be practical, we—the four nations of these islands—one or all, can learn to be plodding and patient, and to appreciate the importance of theory. We may be encouraged in our efforts to do so by the opinions of others, countrymen of Professor Duisberg, eminent in pure or applied science. Professor Ostwald, discussing this subject, said that he was sure the difficulties were considerable only in the beginning (*Journ. Soc. Chem. Ind.*, 1906,

1019), while Professor Lunge, in an address to the Royal Institution (March 15, 1907), made use of the following words:—"Seeing that in pure science the people of Great Britain haver never lagged behind any other nation, and that, on the contrary, the land of Newton and Faraday has been a beacon to all others at more than one epoch, there is absolutely no valid reason why she should now, or at any other time, be behind any other in the combination of science with practice."

Here, indeed, is encouragement, and from one who has had ample opportunity for studying the conditions which obtain in this country. Surely, therefore, we ought to have some confidence in ourselves and try our best to regain a strong and healthy position rather than fold our hands in a spirit of hopeless resignation.

The new Patent Act which came into force this year, and for which the country is so much indebted to the strenuous advocacy of Mr. Levinstein and Sir Joseph Lawrence, seems to many to have inaugurated a new era, and to have removed one of the principal causes of the decline of our chemical industries; if this be so, it is all the more important that the representatives of chemical science should be ready and willing to join hands with the manufacturers in order to assist in the process of regeneration.

The principal changes which have been introduced by the new law are, of course, familiar to all. The most important one, which came into operation on August 28 last, is that which requires that the article or process which is protected by the patent must be manufactured or carried on to an adequate extent in the United Kingdom after the expiration of four years from the date of the patent. If this condition is not fulfilled, any person may apply for the revocation of the patent.

Some of the results of this amendment, and some indications of the great industrial changes which it will bring about, are already obvious. Foreign firms or individuals who hold British patents and who have not sufficient capital to work them in this country, or who do not think they are worth working here, are attempting to sell their British patent rights. Others are building or buying works in Great Britain, and it has been estimated that in the immediate future a sum of at least £25,000,000 of foreign capital will have been thus invested in order to comply with the new law.

We need not stop to consider the economic effects of this transfer of capital on the general trade of this country, but we may well pause a moment in order to try and forecast the consequence of these new conditions in so far as they concern our chemical industries.

The prospective establishment of branches of two of the largest German chemical works at Ellesmere Port and at Port Sunlight respectively are already matters of common knowledge, and it may be presumed that these firms will avail themselves to a large extent of British labour. If this be the case, and if they are successful—as they, no doubt, will be—the complaint that the inferior technical education of our artisans is responsible for our lack of success will thereby be proved to be groundless. Even if we admit that at the present time the British workman is an inferior operative in a chemical works, and only capable of undertaking the less-skilled labour, these firms will gradually raise a considerable number of trained men who will be ready to undertake more responsible duties under our own manufacturers when the good time comes; a school for chemical operatives will be created in our midst, and, as in the past, we shall reap the benefit of knowledge and experience brought to our shores. It also seems reasonable to expect that, as is the case abroad, these works will be equipped with laboratories and staffed by chemists, although possibly only so far as is necessary for routine work. Many of these chemists may settle permanently in our midst, become members of our Chemical Society and Society of Chemical Industry, and thus infuse us with their patience and perseverance. It is not beyond the bounds of possibility that these great firms may even employ British chemists in their works, if we can supply men sufficiently well trained to be of value. On the other hand, as experience seems to have shown that industrial chemistry cannot succeed with imported scientific labour, it is not very probable that many posts in the laboratory will be filled by our countrymen, who, in this connection, must be regarded as foreigners.

Now, at the present time most chemical products can be manufactured more cheaply abroad than here, otherwise we should not have any reason to consider our position. Dr. Duisberg told us that even when an important firm in England had a licence to work all the British patents of two of the largest German colour works, merely paying for the privilege a small percentage of the net profits, it failed to take any advantage of the opportunity. If, then, in this free-trade kingdom production is cheaper than abroad, the foreign firms which have branches here will be in a position superior to that which they now occupy in their own countries. If, on the other hand, owing to inefficient labour, higher wages, freights, and other economic conditions, production is more costly, the superior efficiency and scientific organisation of these foreign firms will nevertheless enable them to command our home market with the goods made here, and to cut us out in the world market, as they do now, with those made abroad.

The conclusion which thus seems forced upon us is, that, although the new Patent Act will prove to be of great value in many respects, it will do little to foster British chemical trade and the development of British chemistry; it places us on an equality with other countries as regards patent rights, and thus remedies an outstanding grievance; but, unless we have something to patent, this equality will be valueless, and our chemical industries will continue to decline, possibly more rapidly than heretofore.

Let us therefore pass in review the other causes which have been suggested as contributory to our failure; after eliminating those connected with freights and tariffs, and with the alleged supineness of the Government in assisting industry, matters which may be left to the manufacturers to deal with, there still remain several which are well within the purview of this Section.

These are:—(1) The unsatisfactory condition of secondary education; (2) the nature of the training which is given to chemists in our universities and other institutions; (3) the insufficiency of the time and money devoted to research in the manufacturing industries; (4) the lack of co-operation between manufacturers and men of science.

There are some who believe that the first of these is the primary, if not the sole, cause of our weakness; that if our secondary education were placed on a sound basis all the other evils would disappear of their own accord; that a steady and broad stream of well-trained boys from the secondary schools would afford ample material from which good chemists could be fashioned in the universities and colleges; that these trained chemists would be greedily seized by the manufacturers, whose minds had been widened by improved educational methods; and once installed in the works these chemists would have no difficulty in persuading their employers to spend time and money on research work in co-operation with the leaders of science.

Whether such desirable and far-reaching results would, in fact, follow if our system of secondary education were very much improved it is impossible to predicate; but there is no doubt that at the present time we are moving in an exactly opposite direction.

The shadow of the cypress rests upon our chemical trade, and manufacturers do not see their way to employ chemists; students are not attracted to chemistry as a profession because there are so few openings; without an ample and increasing supply of such students chemical industry must continue to decline, and as a necessary consequence the development of pure chemistry is cramped and hindered to a far greater extent than is generally realised.

In a Presidential Address to the Chemical Society last year Professor Meldola discussed the position and prospects

of chemical research in Great Britain, and in view of the importance of the subject and the able manner in which it had been treated, the Council of the Society ordered the publication of five thousand copies of his Address for distribution among the members of various public bodies. We were told in this Address that many of our universities are distinct failures as centres of chemical research, and that the output of original work from our colleges, polytechnics, and similar institutions is emphatically not representative of the productive power of the teachers there employed. The causes of the failure of our universities were only lightly touched upon, and I propose to refer to them later; but in the case of our other institutions they were more fully discussed. May I venture to draw attention to one cause, which I believe is by far the most effective drag on research in the vast majority of such institutions not of university rank? It is simply the lack of those more advanced students who, while gaining valuable experience in the methods of research, would also render useful assistance to their teacher. The governing body of the institution may not realise the importance of research; the Principal, as, alas! is sometimes the case, may throw cold water on such work; the teacher may be overburdened with routine duties, and he may be most inadequately remunerated; if, however, the research spirit is strong within him, he would overcome all these difficulties were there any prospect whatsoever of success; but what chance has he when he must do everything himself, even to washing out his own test-tubes? Provide him with a few advanced students, and he would doubtless find time to undertake the necessary pioneer research work, which would then be extended and developed with their assistance.

It might be suggested that an efficient and enthusiastic man would soon attract a number of research students. This, no doubt, is true as regards the universities, but it must be remembered that a polytechnic or other institution which does not grant degrees can hardly expect to compete with a university as a centre for research; all those students who intend to undergo a so-called "complete" course of study—that is to say, all who are likely to become capable of undertaking research work—naturally proceed to one of the degree-giving universities. There are not enough students to go round, to satisfy the research requirements of the teachers, and the principal reason is—the limited demand for trained chemists on the part of the manufacturers.

Even of the small number of those who leave our teaching institutions fairly well trained in research, how many have a chance of passing into works and directly advancing applied science? A very small proportion indeed. Most of the better ones drift into other posts, become demonstrators, emigrate—anything rather than wait on with the prospect of accepting as works-chemist a salary which, meagre though it be, may be stopped altogether if dividends are low.

With whom rests the responsibility for this state of affairs? Is it with the teachers, and, if so, is it because they are incapable of training chemists or because their system is at fault?

To answer this question it is necessary, in the first place, to arrive at some conclusion as to the kind of training which is required for the future works-chemist. On consulting the opinions of the manufacturers it would seem that they attach great importance to what is called the "practical side"; they believe that, in addition to a knowledge of theoretical chemistry, the prospective works-chemist should also have some acquaintance with engineering, should understand the apparatus and machinery used in the particular manufacturing operations with which he is going to deal, and should have had practical experience in working the given process. It is from this point of view that we build and equip large technological chemistry departments, such as those in the Universities of Birmingham and Leeds, and in the Manchester Municipal School of Technology, departments fitted up with complete apparatus and machinery for carrying out operations on a miniature manufacturing scale.

The arguments in favour of this view, that it is a hybrid chemist-engineer who is required in a chemical works, seem to me to be fundamentally unsound, and the kind of training suggested by them for the works-chemist can only result in the production of a sort of combined analytical machine and foreman. A two or three years' course of science, followed by one year's practical work in the dye-house, in paper-making, or in some other technological department, is quite inadequate if the student trained in this way be expected to do anything beyond routine analytical work and supervision.

We cannot possibly expect such a poorly trained Jack-of-all-trades to run a chemical works successfully in the face of competition directed by a large staff of scientific experts in chemistry and in engineering. It is no use spending immense sums of money on expensive machinery of the newest type in order that the works-chemist may be able to tell his future employer that the machinery used in his employer's works is completely out of date. In the course of time, moreover, unless expenditure is practically unlimited, the reverse conditions will obtain, and the technological department of the university or other institution will become more of the nature of a museum of antiquities. The great cost of the upkeep and of the working of such plant is also a very serious matter; is it possible to believe that the educational results of running, say, a large puddling furnace, such as is fitted up in Birmingham University, are in any way commensurate with their cost? The conditions in a chemical works cannot be successfully imitated in a university or polytechnic; attempts to do so can only lead to mistaken conclusions, and thus have the effect of rendering the works-chemist quite helpless when he passes from the elegant models of his educational apparatus to the work-aday appliances of the manufactory.

Here, it seems to me, we touch the bed-rock of our trouble. The state of our chemical industries must be attributed to the erroneous views which have been and still are held as to the functions, and consequently as to the training, of a works-chemist. We have failed to realise that industrial chemistry must be based on a foundation of continuous and arduous research work. In the past we have sent out from our universities and other institutions students who, no doubt, were qualified to undertake routine analytical work, but the great majority of whom knew nothing of the methods of research. We are doing the same to-day. Just when a student has reached a stage at which his specialised scientific training should begin his course is finished, and whether he has been to a university or to a polytechnic matters little; he joins the band of those who subsist on but who do nothing to advance chemical industry. He enters a works; the manufacturer does not realise exactly what his chemist ought to do, but he expects some immediate results, and in consequence is generally disappointed; the lack of success of the chemist is put down to his ignorance of practical matters, and there is an outcry for technical education; science is most unjustly discredited, and any suggestion of spending money on research work is scouted as a mere waste.

The consequence is that there is a scientific problem which intimately concerns all the members of some large industry what course do they adopt? Through their trade journal, and as an association representing a total capital of which I should not like to hazard a guess, they offer a bronze or possibly a silver medal, or may even offer the extravagant sum of £20, to the happy person who will provide them with a solution. It is difficult to imagine the class of solvers to whom these princely rewards may appeal, more difficult still to believe that any useful result can be attained, and it is almost incredible that such methods should be adopted by any influential industrial organisation. This way of attempting to get research work "on the cheap" is certainly not unknown even in

more enlightened countries, but that is hardly a sufficient justification for its employment.

Contrast these methods with those adopted by the Badische Anilin- und Soda-Fabrik, and Meister, Lucius, and Brüning in their attempts to solve the problem of the commercial synthesis of indigo. Could there be a greater antithesis? If five thousand copies of Brunck's Paper on this subject (*Ber.*, 1900, [1], lxxi.) could be circulated among the manufacturers of this country—a task which might be fittingly undertaken by the Society of Chemical Industry—the study of the truly magnificent results attained by the systematic application of pure science, and of the indisputable evidence of their commercial value, might prove an object-lesson far more effective than argument for the accomplishment of a sorely needed reform.

Now if we are to meet successfully the very formidable scientific and commercial organisation opposed to us in chemical industry, we must perforce adopt the methods of our competitors; not only must we learn patience and perseverance, but we must also call to our aid the best brain-power available. We must recognise clearly that the scientific works-chemist, the only man who is likely to make discoveries of commercial value, must be thoroughly trained in the methods of research by those best qualified to do so, and we must not imagine that when he enters the works he should or could immediately become an engineer and a commercial expert; his place is in the research laboratory. The practical man—that is to say, the man who has a thorough and useful knowledge of some particular manufacturing process—must be trained under practical men in the works, and we must not imagine that a course of evening classes will convert him into an expert chemist. The ideal man who combines high scientific training and sound practical knowledge cannot be produced unless the period of his education is extended to half a life-time, and even then only through the co-operation of the chemistry teacher and the manufacturer.

Admitting the truth of these statements—and I do not think that they can be successfully controverted—we have now to consider what steps can be taken to provide these highly trained works-chemists, and to ensure for them a cordial reception on the part of the manufacturers.

The first fact which we have to bear in mind is that the great and rapid development of chemistry in recent times has lengthened the period which is required for the collegiate study of the subject. In order to acquire the necessary knowledge of facts and theory, and afterwards to devote even the minimum time to gaining experience in research methods, the future works-chemist must be prepared to continue at the university or other institution during at least five years. The course of study during the first three years might be on the lines now adopted by many of our universities for the B.Sc. pass examination, but to grant this degree in one or two subjects only, and then to call it an Honours degree, is in my opinion a serious mistake, as is also the admission of research work at this stage, both of which proceedings lead to far too early specialisation. The pass degree should be regarded merely as an indication of a sound general education in science, and the future works-chemist should then devote at least two years more to research and to special work in chemistry, on the results of which the Honours degree might be awarded. Every encouragement in the form of low fees, free admission, research scholarships, and so on, should be offered to such students, according to their merit and circumstances, in order that they may prolong their studies; the cost of these remissions or awards would not be very serious, and the money would be well spent. Teachers should then refuse to recommend, and manufacturers should refuse to employ, as a works-chemist, any student who had not passed through such a course satisfactorily, unless it was understood that he was only expected to undertake routine analysis, or work outside the research laboratory. By thus extending the period of training, and making research work compulsory as far as possible, a great deal would be gained; pure science would reap an immediate benefit from the investigations of the students—as has been the case abroad—and this stimulus would necessarily react on industrial chemistry; the manufacturers could be assured that they were being supplied with men of the right type; they would soon come to recognise that fact, and the demand for works-chemists would expand. In the laboratory of the works the manufacturer would then have the opportunity of gauging the capabilities and special leanings of every chemist on his staff. Those who were best fitted for directing operations in the works could be trained on the spot, as they could not possibly hope to be trained in any university or polytechnic; those who proved to be the best research chemists would, of course, remain in the laboratory working out scientific problems. Organisations of this kind could not fail to command success, and the opsonic curve of our chemical industries would soon begin to rise.

There is one institution, not a teaching body, which might greatly assist in this movement; I refer to the Institute of Chemistry of Great Britain and Ireland. This body desires and claims to represent chemistry, not only in these islands, but in all our dominions, and also to exercise some supervision or control over public appointments. It examines in chemistry and grants diplomas, and claims that its examinations are a test of practical ability rather than of theoretical knowledge. I have not a word to say against the character of these examinations, but to imagine that the Institute of Chemistry qualification is the hall-mark of a chemist is ridiculous. An average student can obtain the diploma after three, or at the very most four, years' work subsequent to matriculation, and more easily than the London B.Sc. (external). Here, again, it should be recognised that the present Institute of Chemistry qualification is only a step in the training of a chemist; the permission to present a thesis for the Associate examination should be withdrawn, and good research work should be insisted on in the case of all candidates for the Fellowship. It would then be possible to distinguish between those who are capable routine chemists and those who might be expected to advance pure and applied science. It is certainly a grave matter for an Institution entirely controlled by chemists to set such a bad example by ignoring the necessity of research work; if all our official chemical appointments and many of our posts in works are to be filled by men who have done no independent scientific work the results will be most serious; the research habit and the research method are not easily acquired without assistance, and therefore it is all the more important to make use of this assistance while it is within reach, and before the budding chemist begins to believe that he has nothing more to learn.

As a necessary corollary to making research compulsory in the training of works-chemists, all our important teaching institutions must afford ample opportunities for such work, and measures must be adopted to guard against that failure of some of our universities as centres of research which was pointed ont by Professor Meldola.

Such failure, whatever may be the contributory causes, must be principally due to the absence of sufficient interest in research work on the part of the professor, and it certainly seems surprising, at first sight, that in these days many such professors are to be found; but it must be remembered that, although by members of this Section research work is regarded as the highest and most important of all professorial duties, this is not always the view of those who make an appointment to a Chair.

In selecting a professor there are many other considerations which come into play: his ability as a teacher in the class-room and laboratory; his qualifications as a popular exponent of science; his power of organisation; his bearing towards his colleagues and his students—all these matters are of great and direct importance to a university, and it is not to be wondered at that a man highly qualified in these accessories may sometimes be chosen even though he may take no special interest in research work.

The results of such an appointment, however, cannot fail to be most prejudicial to the highest interests of the university and of the country; the chemistry department becomes a chemistry school, but not a school of chemistry.

Unfortunately, moreover, the results extend over a long period; this raises another question which certainly requires attention if we are to become more efficient.

It is far from my object to create any gratuitous insecurity of tenure in chairs of chemistry, but it is not desirable that in our teaching institutions the conditions of all appointments should include a superannuation clause? Not that a rigid age-limit should be introduced, but there should be a possibility of bringing about the retirement of those who for any reason can no longer adequately fulfil their duties. When, owing to the lapse of time, such retirement became necessary, the aged and honoured professor, pensioned by a grateful university, might still retain an intimate connection with its scientific life; as emeritus professor, with a research laboratory at his disposal, he might remain to advise and encourage his youthful successor even when the duties of teaching and the general supervision of a department had become too arduous.

It cannot be suggested that my remarks on this delicate topic are inspired by the impatience of youth or by freedom from personal consequences; the time when superannuation becomes desirable may arrive for one and all, and I have ventured to draw attention to the matter simply and solely because of its grave importance in connection with the subject of my Address. The country cannot afford to allow periods of inactivity or decadence in our seats of learning, and the interests of the individual must be subordinated to those of the nation.

Even if by adopting the above suggestions the training of our chemists is improved, and all our higher educational institutions become permanent and active centres of research, the manufacterers may still remain unresponsive, what can be done in other ways to bring about the active co-operation of pure and applied science?

The great proportion of the original work now done in this country, judging from the published records, is absolutely free from any utilitarian bias; the time, brain-power, and money devoted to this work are considerable, and the results from a scientific point of view eminently satisfactory. If even a fraction of the same skill and energy were brought to bear under proper conditions on problems of applied science, who can doubt but that the effect on our chemical industries would be one of vast importance? And yet it is the rarest possible occurrence to find any record of research work undertaken with a commercial object even in the natural home of such records, the *Journal of the Society of Chemical Industry*.

One reason for this may be that the discoveries made in the works-laboratories are not given to the world at large, but are quietly and lucratively applied in some secret manufacturing process. Another reason, unfortunately the more probable one, may be that nearly all the principal research workers are completeiy shut off from any industrial influences.

Now the worker in pure science, unaided by the advice of the manufacturer and business man, has little chance of solving any important technological problem, except as the result of accident; he has not the requisite acquaintance with commercial conditions, does not realise the enormous difference between operations on the laboratory and the manufacturing scales, or, if he does so, is unable to enter fully and with confidence into questions of fuel, labour, and so on, which often determine the success or otherwise of a process. Further, much of the research work of direct commercial value concerns methods for reducing the cost of processes already in operation, and demands an intimate practical knowledge of these processes.

It is obvious therefore that, even if all the research capacity of the country were henceforth devoted to purely technical matters, any great improvement in our industries could hardly be anticipated without the active co-operation of the manufacturers.

Now it has been stated (Levinstein, *Journ. Soc. Chem. Ind.*, 1903, 845) that the authorities of the Manchester Municipal School of Technology intend to undertake investigations for local manufacturers and merchants in connection with difficulties which may be met with in their works or business. This method of securing the interest and support of those engaged in applied chemistry may or may not be workable according to the conditions under which such co-operation is carried out. The staff and the laboratories of a university or polytechnic cannot be placed at the unrestrained and gratuitous disposal of any manufacturer who is in some trivial difficulty, nor can the choice of the subjects to be investigated be decided by the governing body. If, however, the arrangements, pecuniary and otherwise, are left entirely in the hands of those directly concerned, namely, the manufacturer and the responsible head of the chemistry department, the scheme should then prove exceedingly valuable, and should be adopted as widely as possible. It should be understood, and the fact might even be advertised by the governing body, that for purposes of research work in applied chemistry—but not, of course, for analytical work—the laboratory of the university, college, or polytechnic is, under certain conditions, at the service of the manufacturers; that although primarily and unswervingly devoted to work in pure science, such institutions recognise that, for their own interests, they must do all they can to assist chemical industries.

It might be thought that these conditions prevail at the present time and that any manufacturer, if he so choose, may consult the university staff on any problem in which he is interested. Possibly this is true to a limited extent, but in most institutions the members of the staff are restrained from undertaking any outside work; in others, such work may only be done with the sanction of the authorities.

These conditions, of course, are only laid down because the governing body believes that they safeguard the interests of the institution, and if it were shown that their enforcement is really contrary to those interests they would soon be abrogated. Many or all such authorities readily permit the members of their staff to undertake outside examination work because they consider this course to be to the advantage of their institution; but how incomparably more important is the object of gaining the confidence and support of the manufacturers.

Pray do not let it be imagined that this is some subtle scheme for increasing the pecuniary rewards of the teachers. I greatly fear that to many of those who are now engaged in research work the suggestion that they should give some attention to applied chemistry would be very distasteful, simply because it would involve an immediate encroachment on the time, already far too limited, which they are able to give to the immediate scientific problem which is one of their principal joys in life. To those who might have fears of this kind I would point out that there would soon be some compensation; once the co-operation of the manufacturers is secured, the demand for research chemists would expand, and the laboratories would be filled with students whose help in pure science would be invaluable.

The possible objection that the teaching staff would devote too much time to applied work and neglect other duties is one which could be left for the governing body to deal with unsparingly. If the institution took some percentage of all extraneous remuneration, or any similar arrangement were made, the funds thus provided could be used for increasing the staff of assistants and demonstrators—a most desirable reform in itself.

One of the greatest advantages of a working arrangement such as that here indicated would be that, like the method already suggested, it would lead to the evolution of what is otherwise almost unattainable—namely, men thoroughly trained in both science and practice. The research students of the teaching institution, engaged on a given problem for a manufacturer, would of course be allowed to study its practical aspects in the works; on the

other hand, works-chemists, with considerable practical experience, would be granted permission to proceed to the university laboratory, where they would study the problem with the assistance of the highest scientific knowledge, and acquire further training in the methods of research.

Combinations such as these could hardly fail to lead to valuable results, which would form the subject of patents; the monopolies thus acquired would place the manufacturers in a favourable position, and the revival of our chemical industries would follow in due course. There is nothing Utopian in this scheme, and there are no great initial difficulties to be overcome; it may be set in operation by the manufacturer, and possibly also, as will be indicated later, by the worker in pure science. Reading between the lines certain records which have recently appeared in the science journals and the patent lists, it may even be inferred that such arrangements are already in force in one of our large industrial centres.

There are other ways in which it might be possible to obtain the active co-operation of the manufacturers. Any individual or firm interested in a problem of applied science might be invited to found a temporary research scholarship at the university or other institution for the definite object of the particular problem in question. The maximum period during which such a scholarship would be tenable might be fixed beforehand, so that the financial liability of the founder would be limited and proportionate to the importance of the object in view. The holder of the scholarship might be nominated by the university, or by the founder and the university jointly, and suitable conditions would be drawn up to ensure the interests of the founder; he would of course have the benefit of all the results of the work, and would secure the patent rights of any new invention, subject possibly to the payment of a small percentage of the profits to the university and to the holder of the scholarship. During the tenure of the scholarship, the holder, and also the founder, would have the advantage of the scientific knowledge of the university; the scholarship holder would also be allowed to gain practical experience in the works, and, if successful, there is little doubt but that he would have the option of working the process on the large scale and of obtaining permanent employment under satisfactory conditions. After a given period the scientific results of the work would be published through the usual channels in the ordinary way.

This idea of applied research scholarships had taken shape in my mind when I happened to come across a book recently published in the United States, called "The Chemistry of Commerce," in which I found that a similar proposal had been made by the author, R. K. Duncan, Professor of Industrial Chemistry at the University of Kansas. The scheme is there worked out in some detail, and a form of legal agreement to be signed by the university authorities and by the founder of the "Industrial Fellowship" is suggested.

Thinking it would be of interest to know how the plan had worked out in practice, I wrote to Professor Duncan and received a reply a few weeks ago. He very courteously informed me that five industrial fellowships had already been established in his laboratories, that the agreements for two additional ones were being prepared, and that he might have obtained more but wished to proceed conservatively; also that he had no reason to doubt the entire practicability of the scheme, and that experience had shown that the terms of the agreement could be made more favourable to the university than those which were first drawn up. One of the new conditions is that the industrial fellowship holder shall give two hours a week gratuitous instruction in the work of the chemistry department—an arrangement which has proved to be of great inspirational value. The fellowships are tenable during two years and are of the value of 500 dols. or 1000 dols. per annum.

It is too soon to be able to form any opinion as to the commercial importance of the work carried out under this scheme, but it is obvious that the foundation of such scholarships for the study of general or special problems in applied chemistry is most desirable. One of their great advantages would be that they might be founded by those manufacturers who cannot afford permanently to engage a research chemist. Large and successful firms like the United Alkali Co., Brunner, Mond, & Co., and many others which can employ a staff of chemists, are of course eminently capable of managing their own affairs without outside assistance or advice, and it is only for those which are less prosperous that the foregoing suggestions are made.

The great benefits which are conferred on pure science by the open research scholarships at present available afford some indication of what might be done for industrial chemistry by the foundation of such scholarships in applied science. There are, no doubt, scattered over the country many men who possess originality and inventive talent, and who have practical experience in industrial operations, but who have not been sufficiently trained in science; if it were possible to attract this dormant talent by means of open scholarships it might be directed into proper channels instead of being allowed to run to waste.

It is easy to say how money might be spent advantageously, but very difficult to suggest how the funds for such open scholarships should be raised. An appeal to the manufacturers by this Association or by the Society of Chemical Industry might meet with some response, and it is also possible that public bodies might render assistance. If the Government of Bengal, under the spur of dire necessity, can subsidise research work on indigo, and if our county councils can offer scholarships for dairy work, and grants for experiments on turnip-growing, bee-keeping, and so on, our city and borough councils might award scholarships in applied chemistry for subjects of especial importance to the dominant trades of the district. By so doing they would be utilising to the best advantage the chemistry departments of our universities and polytechnics.

I noted a few moments ago that practically all the published research work of this country has no direct reference to any industrial problem; nevertheless the results of this work are often of such a character that they might be of considerable technological importance. New reactions are discovered; new or improved methods of preparing known compounds; new facts as to the conditions under which important general reactions occur; and, needless to add, a great many new compounds are prepared.

Now, abroad, all or nearly all such matters are protected by patents, generally taken out by some firm of manufacturers. To the uninitiated it seems absurd to think that there is money in the great majority of such patents, and yet it is obvious that the employment of this system must pay in the long run. Why should it not be adopted in this country—at any rate to a limited extent to start with?

If all those who are engaged in purely scientific research work would seriously consider the desirability of obtaining provisional protection for any discovery which they may make, and would then consult some manufacturer or industrial expert with whom the further development of the matter might be undertaken, there is reason to believe that in some cases at least the patent might prove to be a commercial success.

The examination of the therapeutic action of compounds discovered in our laboratories is also a possible means of assisting our chemical industries; the matter is not so trivial as it may seem; a monopoly in the manufacture of some valuable medicinal preparation would serve as a *point d'appui* from which more important operations could be undertaken.

Unfortunately the investigation of the physiological action of new preparations is a matter of some difficulty in this country, as it is to some extent connected with vivisection in the public mind; we may poison rats with impunity, and even create an organisation for their extermination, but we may not individually try the effect of a new compound on a rabbit.

In drawing this address to a conclusion I cannot but

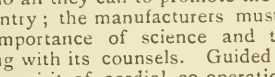
feel that my suggestions may seem utterly inadequate to the attainment of those important results which are so greatly to be desired. If so, I can only plead that more drastic measures are hardly available, and that even under the most favourable circumstances improvement can take place only very slowly. Whatever differences of opinion may be held as to the details of any scheme for regaining our lost ground, the main lines seem to be clearly indicated. The workers in pure science must recognise that it is their duty to do all they can to promote the industrial welfare of their country; the manufacturers must concede the paramount importance of science and the impossibility of dispensing with its counsels. Guided by these principles and by a spirit of cordial co-operation, a sustained and strenuous effort on the part of the leaders of chemical industry and of chemical science can hardly fail to accomplish the end in view.

In elaborating this Address I have enjoyed the advantage of the criticisms and suggestions of my friend and relative Professor Perkin, F.R.S., to whom my sincere thanks are here expressed.

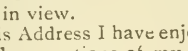
THE ISOMERISM OF ETHYL ACETO-ACETATE.

By R. H. McCREA.

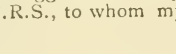
In the general theory of the stereo-isomerism of unsaturated compounds the following types are met with :—



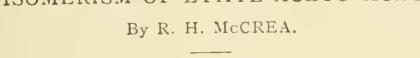
and it appears that by a slight extension of this the case of aceto acetic ether may be covered. If we represent the formula for the enolic form, $CH_3.C(OH):CH.COOEt$, by the graphic method (II.) above,—



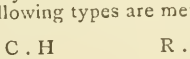
we see at once that the *cis*-configuration corresponding to this is—



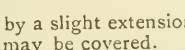
Now, in the case of the Beckmann transformation the following has been thought to be the probable course of the change (Bernthsen) :—



There does not seem, then, any difficulty in supposing the *cis*-modification unstable in the case of the ethyl ester, for—

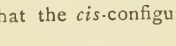


corresponds exactly with the hypothetical intermediate product above, and gives at once—



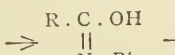
the ketonic form of the ester, by a change in the position of the double bond, the hydrogen atom of the hydroxyl changing over to the carbon atom, and the oxygen of the hydroxyl taking possession of the free affinity, just at the moment when the *cis*-position is attained. Afterwards, of course, there is free rotation about the single bond linking the carbon atoms.

Now, with phosphorus pentachloride β-chlorocrotonic acid is formed, $CH_3.CCl:CH.COOH$, which may be represented as either—



We should here be led to expect that both modifications would be stable, for there is no element present in the chlorine radical to saturate two links of the carbon atom like the oxygen of the hydroxyl in the supposed unstable *cis*-modification of ethyl aceto-acetate. Nor is this expectation unsupported by facts, for the above chloro-compound yields isocrotonic acid, $CH_3.CH:CH.CO_2H$, under the action of sodium amalgam, which is taken as being stereo-isomeric with ordinary crotonic acid.

To the question as to which of the modifications, stable or unstable, of the ethyl ester should be regarded as the *trans*- or *cis*-form no answer is attempted. For convenience one form has been adopted above, but the other would serve the purpose equally well. It may be pointed out, however, that while the configurations of the crotonic acids have not been settled apparently, the *iso*-acid is formed from the chloro-*iso*-acid, which also gives rise to tetrolic acid, $CH_3.C{:}C.CO_2H$, by the loss of hydrogen chloride in presence of aqueous potash. Now, although the loss of a H and Cl atom does not necessarily imply that these are spatially near each other, if such were found to be the case, in this instance we could work backwards, thus,—



The latter form in the case of the ester might perhaps be regarded as the stable hydroxy configuration.

Chesterfield, July 21, 1908

THE ELECTROLYTIC PROPERTIES OF DILUTE SOLUTIONS OF SULPHURIC ACID.*

By W. C. D. WHETHAM, M.A. F.R.S., and H. H. PAINE, B.A., Trinity College, Cambridge.

(Continued from p. 120).

Part II.—*By* H. H. Paine (*continued*).

Table II. contains the results of the whole series of experiments; its various columns will easily be understood from the preceding example. In deducing the mean of the several values for the migration constant at any particular concentration, those experiments were regarded as most trustworthy for which the calculated changes at anode and cathode were most nearly equal, and the values for the migration constant were weighted accordingly. The difference between the weighted mean and the actual one was always quite small.

The solution 0·0001 normal was the strongest for which the conductivity could be measured in the migration cell itself. Hence, for the solution 0·0002 normal in the case of which the anode and cathode portions had to be transferred to the conductivity cell, and for which the discrepancies between the changes on the two sides were rather large, the value obtained for the migration constant is not very trustworthy. Of the three experiments performed with this solution, that showing the best agreement between the measured changes at the anode and cathode is the one giving 0·188 as the migration constant.

It was found that the conductivities of solutions of the same strength made up with different specimens of distilled water were not the same. When the discrepancy was small, the procedure adopted in calculation was as follows :

* A Paper read before the Royal Society, June 18, 1908.

TABLE II.

I. No. of solution.	II. Initial concentration (grm.-equivalent per litre).	III. Total change in quantity of H_2SO_4 (grm.-equivalent). Anode.	IV. Cathode.	V. Mean.	VI. Grm.-equivalent of hydrogen liberated at cathode.	VII. Migration constant from Columns V. and VI.	VIII. Weighted mean.
1.	$1{\cdot}0465 \times 10^{-1}$	$4{\cdot}47 \times 10^{-4}$	$4{\cdot}67 \times 10^{-4}$	$4{\cdot}57 \times 10^{-4}$	$2{\cdot}485 \times 10^{-3}$	0·184	
2.	1·0465 ,,	5·71 ,,	5·83 ,,	5·77 ,,	3·079 ,,	0·187	
							0·186
3.	$1{\cdot}0070 \times 10^{-1}$	$5{\cdot}82 \times 10^{-5}$	$6{\cdot}14 \times 10^{-5}$	$5{\cdot}98 \times 10^{-5}$	$3{\cdot}214 \times 10^{-4}$	0·186	
4.	1·0070 ,,	8·65 ,,	8·96 ,,	8·80 ,,	4·744 ,,	0·1855	
							0·186
5.	$1{\cdot}0230 \times 10^{-3}$	$5{\cdot}50 \times 10^{-6}$	$5{\cdot}71 \times 10^{-6}$	$5{\cdot}60 \times 10^{-6}$	$2{\cdot}71 \times 10^{-5}$	0·206	
6.	1·0230 ,,	5·49 ,,	5·64 ,,	5·56 ,,	2·96 ,,	0·188	
7.	1·0255 ,,	5·49 ,,	5·51 ,,	5·50 ,,	2·93 ,,	0·188	
8.	1·0255 ,,	4·09 ,,	4·13 ,,	4·11 ,,	2·13 ,,	0·193	
9.	1·0165 ,,	3·37 ,,	3·49 ,,	3·43 ,,	1·864 ,,	0·184	
10.	1·0165 ,,	3·52 ,,	3·48 ,,	3·50 ,,	1·864 ,,	0·188	
11.	1·0165 ,,	3·90 ,,	3·92 ,,	3·91 ,,	2·11 ,,	0·185	
							0·189
12.	0·5133 ,,	2·57 ,,	2·59 ,,	2·58 ,,	1·402 ,,	0·184	
13.	0·5133 ,,	3·77 ,,	3·83 ,,	3·80 ,,	2·05 ,,	0·185	
14.	0·5081 ,,	2·89 ,,	3·02 ,,	2·955 ,,	1·582 ,,	0·187	
							0·185
15.	0·20785 ,,	0·644 ,,	0·596 ,,	0·620 ,,	$3{\cdot}40 \times 10^{-6}$	0·182	
16.	0·20785 ,,	1·008 ,,	0·963 ,,	0·985 ,,	5·25 ,,	0·188	
17.	0·20785 ,,	1·100 ,,	0·022 ,,	1·061 ,,	5·70 ,,	0·184	
							0·1855
18.	$1{\cdot}0140 \times 10^{-4}$	$5{\cdot}765 \times 10^{-7}$	$5{\cdot}625 \times 10^{-7}$	$5{\cdot}695 \times 10^{-7}$	2·93 ,,	0·195	
19.	1·0140 ,,	5·15 ,,	5·18 ,,	5·165 ,,	2·69 ,,	0·192	
20.	1·0140 ,,	6·65 ,,	6·55 ,,	6·60 ,,	3·38 ,,	0·195	
							0·194
21.	0·5440 ,,	3·18 ,,	3·25 ,,	3·215 ,,	1·566 ,,	0·205	
22.	0·5440 ,,	3·78 ,,	3·78 ,,	3·78 ,,	1·827 ,,	0·207	
23.	0·5405 ,,	2·83 ,,	2·83 ,,	2·83 ,,	1·392 ,,	0·203	
24.	0·5405 ,,	3·01 ,,	3·08 ,,	3·045 ,,	1·522 ,,	0·200	
25.	0·5832 ,,	2·62 ,,	2·56 ,,	2·59 ,,	1·359 ,,	0·191	
26.	0·5832 ,,	5·58 ,,	5·50 ,,	5·54 ,,	2·756 ,,	0·201	
							0·202

—From the conductivity of the solution a value for the concentration was calculated from the curve which had been already drawn. Let m be this value, and m_0 the true concentration. Then, from the standpoint of the conductivity curve, m_0 gramme-equivalents behave as though they were m gramme-equivalents. Hence, concentrations deduced from the curve were multiplied by the factor m_0/m to get the true concentrations. We get practically the same result, if, calculating k/m_0 for the solution, we increase or decrease the ordinates of the curve (by some fixed length) until it passes through the point showing the true value of k/m for the solution, and calculate concentrations from this curve. The corrections made in this way were only small ones, so that, though the method of correcting has no very firm theoretical basis, it is probably accurate enough for the purpose.

In the case of one or two of the weakest solutions made up six or seven weeks after the rest of the experiments had been performed, the discrepancy was rather large. For these solutions fresh conductivity curves were plotted (from direct experiment) which passed very near the points corresponding to the new solutions, and from these curves the "final concentrations" were calculated for these solutions.

It will be noticed that some of the values for the transport ratio are abnormally divergent from the mean. There was nothing in the course of these particular experiments to lead one to regard the results as untrustworthy. An explanation of the divergence will be suggested later. In deducing the "mean" of the results of individual experiments, however, no account was taken of this explanation; the final results therefore are purely experimental.

5. *Theoretical Considerations.*

These experiments seem to show an increase in the migration constant at extreme dilutions. If this be due to the falling-off in velocity of the hydrogen ion, we can calculate what the rise in the migration constant should be in order to account for the drop in the equivalent conductivity curve. To do this, it is necessary to make some assumption as to the cause of the smaller velocity of the hydrogen ion, and so deduce what the conductivity would have been if the velocity had remained unaltered. It has long been noticed that the phenomenon under investigation is observed only for acids and alkalis; *i.e.*, those substances which in solution form hydrogen or hydroxyl ions, the ions of the solvent. Considerations of mass action show at once that the ionisation of the water is greatly reduced by the presence of a trace of acid or alkali. The greater the concentration of the acid, the smaller will be the ionisation of the water. Assuming that the conductivity of Kohlrausch's purest water ($0{\cdot}87 \times 10^{-7}$) gives us approximately a measure of its ionisation in these conditions, it may be shown that for concentrations of acid or alkali greater than 10^{-7} grm.-equivalent per litre, the number of hydroxyl or hydrogen ions from the water is inversely proportional to the quantity of acid or alkali in solution.

If the diminution in the equivalent conductivity of acid solutions at extreme dilutions be caused by the water itself rather than by impurities, it is reasonable to suppose that the effect would be directly proportional to the ionisation of the water, and hence inversely proportional to the concentration of the acid, the effect becoming greater as the dilution proceeds. Now, if at points along the equivalent conductivity (k/m) curve, we add ordinates proportional to the concentration of the hydroxyl ions (*i.e.*, inversely proportional to the concentration of the acid) we obtain another curve. For one particular proportionality, and one only, this curve gradually becomes horizontal as it approaches the axis for zero concentration; that is, it neither dips nor rises. If the proportionality be greater than this critical value, the curve would rise more and more rapidly, while if a smaller proportionality be taken, the

curve would descend (in a manner similar to the actual experimental curve). It seems feasible as a working hypothesis, to regard the critical curve so obtained as giving us the k/m curve which would have indicated the conductivity, had the ionisation of the water remained unaltered.

We can now calculate the change in the migration constant which results from the diminution in conductivity—assuming that diminution to be due to the decrease in velocity of one of the ions.

Let u and v be the velocities of the anion and cation respectively, u being variable. Then at any particular concentration, the conductivity k of the acid is equal to $c(u+v)$, where c is a constant. The transport ratio μ for the anion is equal to $v/(u+v)$. Thus μk is equal to cv, and is therefore constant.

Let μ_1 and k_1 refer to the experimental curve, and μ_2 and k_2 to the theoretical one. We regard μ_2 as remaining constant. Its numerical value is obtained from experiments on solutions for which k_1 and k_2 are practically equal, for then $\mu_2 = \mu_1$. For any particular concentration we now have k_1, k_2, and μ_2; hence, μ_1, the actual migration constant, is obtained.

The process described above, of plotting the theoretical curve, was carried out with the k/m curve given in the paper already referred to (Whetham, *Roy. Soc. Proc.*, 1905, A, lxxvi., 582). Since certain impurities have a considerable effect in lowering the conductivity, it seemed feasible to take the highest curve which consistently resulted from experiment, and regard the lowness of others as being due to impurities.

Table III. gives the values then obtained, the value of μ_2 being taken as 0·186.

Table III.

Concentration (grm.-equiv. per litre).	k_2 (theoretical).	k_1 (experimeutal).	$u_1 = \frac{k_2}{k_1} u_2$.
0·001	367	365	0·187
0·0005	378	374·5	0·1875
0·0002	387	378·5	0·190
0·0001	389	373·5	0·1935
0·00005	390	358·5	0·2025
0·00003	390·5	339·5	0·214

The "theoretical" migration curve, plotted from the figures in the last column of Table III., is shown in the diagram (Fig. 4) as a smooth line, and the experimental values obtained (Column VIII. of table in § 4) are indicated by crosses.

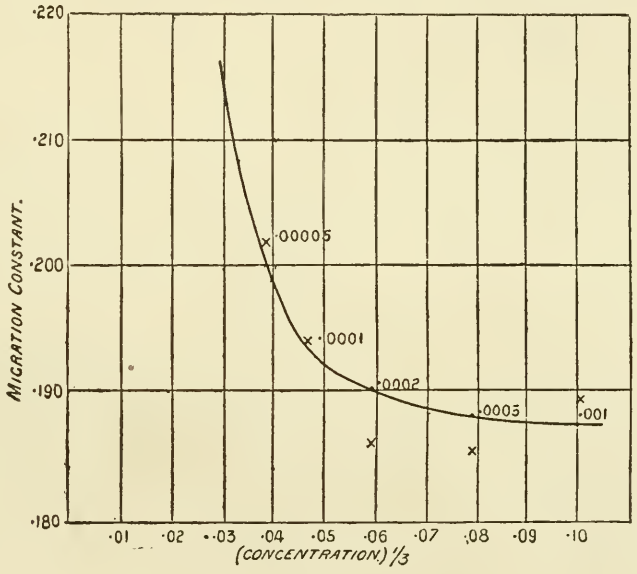


Fig. 4.

§ 6. It was thought at first that these experiments gave fresh evidence in favour of the theory that the velocity of the hydrogen ion is diminished at extreme dilution, and that this diminution accounts for the drop in the k/m curve. The extent of the change observed in the migration constant seemed strongly to favour this explanation. Further examination, however, including a calculation of the effect of impurities, shows that the theory receives no support from these experiments, the whole of the rise attributed to the migration constant being readily accounted for, when we take into consideration the residual conductivity of the water. Let us then consider the problem from the standpoint of a supposed unaltered migration constant.

Let us imagine the conductivity of the distilled water to be due to the presence of some substance A B which becomes ionised in the solution. For all the substances likely to constitute this impurity, hydrogen will be evolved at the cathode, and oxygen at the anode, when the solution is electrolysed. As in the electrolysis of sulphuric acid, the total quantity of solute will remain constant, and the change at the anode will be balanced exactly by that at the cathode. Consider a solution of sulphuric acid containing m grm-equivalents of the acid per cubic centimetre, and let there be, in this solution, n grm.-equivalents of the substance A B in the ionised state.

Let u be the velocity of the H ion, v of the (SO_4) ion, u' of the A ion, v' of the B ion; we have $u = 319$, $v = 73$, as deduced from the "limiting" equivalent conductivity and the migration constant of sulphuric acid.

The conductivity of the solution is $m(u+v) + n(u'+v') = K$, say. Suppose 1 grm.-equivalent of hydrogen to be liberated at the cathode. Distributing the conductivity amongst the several ions, we deduce the following changes in the anode region:—

mv/K, grm.-equiv. of SO_4 ions enters; nv'/K, grm.-equiv. of B ions enters.

mu/K, grm.-equiv. of H ions leaves; nu'/K, grm.-equiv. of A ions leaves.

Also by the action on the water of the SO_4 and B ions, liberated at the anode, 1 grm.-equivalent of H ions ar formed. Hence, in the anode region, there is a net gain

of H ions amounting to $\{mv+n(u'+v')\}/K$ grm.-equivalent.

Hence the total conductivity of the solution at the anode is increased by the amount—

$$[mv \,.\, v + nv' \,.\, v' + \{mv + n(u'+v')\}\, u + nu' \,.\, u']/K,$$

which is—

$$\{mv(u+v) + n(u'+v')(u+v'-u')\}/K.$$

If instead of drawing the "equivalent conductivity" curve in the usual way, we plot the specific conductivity (k) against the concentration (m), we shall find that the curve so drawn is a straight line (not passing through the origin). Hence the increase in conductivity is interpreted as being directly proportional to the increase in the concentration, and consequently (for equal quantities of hydrogen evolved at the cathode) directly proportional to the migration constant, as measured in these experiments.

For pure water and sulphuric acid, $n=0$, and the increase in the conductivity becomes $mv(u+v)/m(u+v) = v = 73$.

The conductivity of the water used was about 10^{-6}. Let us regard this for the moment as being wholly due to the impurity present. For acid substances, like carbonic acid, which are only slightly ionised and have an ion in common with sulphuric acid, this number must be reduced to indicate the conductivity of A B in the acid solution, as the presence of the sulphuric acid diminishes the ionisation of carbonic acid. For the corresponding saline substances (sulphates) the suppression would be inappreciable.

1. If the impurity be free acid, we have $u = u'$, and the above expression reduces to $\{mv(u+v)+nv'(u+v')\}/K$. For the weakest solutions of sulphuric acid used, the conductivity was 18×10^{-6}, so that—

$$m(u+v) = 18\times10^{-6},\ n(u+v') = 1\times10^{-6}.$$

Hence the expression for the increase in conductivity becomes—

$$(18v+v')\times10^{-6}/19\times10^{-6},$$

which is never much greater than v, since there are no anions (with the exception of the hydroxyl ion) which have a velocity appreciably greater than that of the sulphate ion. Hence the increase in conductivity at the anode, and the decrease at the cathode, is never appreciably greater than it is when no such impurity is present. With ions for which $v'<v$, the migration constant would appear to be diminished. The extreme effect for the above concentrations of sulphuric acid would be 1 part in 19 (*i.e.*, $v'=0$), reducing the measured value of the migration constant from 0·186 to 0·176. For any real ions, however, v' is never less than about 40, so that the migration constant would never appear to be less than about 0·182. For very weak acids (*e.g.*, carbonic acid) all such effects are very much reduced, as their "partial conductivity" would be much less than 10^{-6} in the presence of the sulphuric acid. We may conclude, therefore, that the presence of acid impurities in the water used as solvent cannot explain the large increase observed in the migration constant.

2. If the impurity in the water consisted of free alkali, it would be neutralised by the acid, the hydroxyl and hydrogen ions disappearing from solution. We shall find that, though the presence of traces of salt, such as potassium chloride, has no effect on the partial conductivity of the acid, yet it has a very pronounced effect upon the transport ratio as measured in the previously described experiments.

As before, we have the formula for the increase in conductivity at the anode,—

$$\{mv(u+v)+n(u'+v')(u+v'-u')\}/K.$$

Since $u(=319)$ would always be large compared with $(v'-u')$, we may get an approximate value for this expression, writiting it—

$$\{mv(u+v)+nu(u'+v')\}/K.$$

Since H and (OH) ions are excepted, v' and u' even in extreme cases, would never differ by more than 30, and hence the maximum error we introduce by taking this approximation is about 1 in 50, thereby making the transport ratio uncertain to the extent of three or four units in the third decimal place. On the theory to be suggested later, there is practically no difference between v' and u', so that the approximation is nearly exact. Putting in the values as before, we get—

$$\{18\times10^{-6}\times73+319\times10^{-6}\}/\{18\times10^{-6}+10^{-6}\} = 86.$$

Hence for a solution of this strength, the migration constant appears to be increased in the ratio 86/73; *i.e.*, from 0·186 to 0·219.

This rise is greater than that actually observed. Hence, to explain the experimental results, it is only necessary to assume that about half the conductivity of the water used is due to (alkaline or) saline impurity. That such impurity should be present is more than likely; if present, its effect as described above is certain.

The physical explanation of the result of the above analysis is as follows:—If the conductivity of the water (10^{-6}) were due to the presence of sulphuric acid, the migration constant would be unaffected. When the ion A replaces the hydrogen ion, a much larger number of molecules (between three and four times as many) is required to make up the initial conductivity, 10^{-6}. Hence, in the migration, between three and four times as many B ions enter the anode region as before. Since the increase in conductivity of the solution at the anode is nearly proportional to the number of SO_4 and B ions entering the region, and since the proportion of B ions to SO_4 ions for these concentrations of sulphuric acid is quite appreciable, and the velocities of the two ions of the same order, it follows that we should expect a marked effect on the change in conductivity from which the migration constant is deduced.

§ 7. The experimental results obtained, therefore, gave no evidence in favour of the rise in the true migration constant of sulphuric acid at extreme dilutions; the whole of the apparent rise can be explained logically in a more simple way. In fact, these experiments point rather to a constant value for the transport ratio, though they would not be inconsistent with a gradual decrease in that ratio.

The above analysis also explains why the results for individual experiments sometimes varied rather widely from the mean; the supposition that a slight variation in the amount of impurity occurred, owing to the absorption of ammonia from the air, for example, being sufficient for the purpose. Also, it was noticed throughout the research, though the fact had to be left unexplained at the time, that experiments performed with different portions of the same prepared solution, generally gave results which agreed better amongst themselves than with those deduced from the use of other specimens of solution of practically the same strength. That still greater irregularity was not shown is accounted for by the fact that the various specimens of distilled water were always prepared in similar conditions, and the conductivity never varied more than 1 part in 20 from the average.

(To be continued).

CORRESPONDENCE.

THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

SIR,—I am in entire accord with Dr. Divers that the Chemical Society is not a qualifying body. Is it too late for the Society to state this fact publicly?

It has been urged to do so for many years, and until it does, dishonest use of its Fellowship will continue.—I am, &c.,

BERTRAM BLOUNT.

70—78, York Street, Westminster,
August 26, 1908.

NOTICES OF BOOKS.

Leather Industries Laboratory Book. By H. R. PROCTER, M.Sc., F.I.C., F.C.S. Second Edition. London: E. and F. N. Spon, Limited. New York: Spon and Chamberlain. 1908.

ALTHOUGH described as a laboratory book there is much in this work which distinguishes it from the typical practical text-book and gives it a special value as a treatise on analytical principles; the descriptions of experimental processes are clear and detailed, and in all cases the preliminary discussions of the experiments would repay very careful study before the actual laboratory work is begun; these discussions, *e.g.*, that on the chemistry of tannins, contain in most cases all that it is essential for the leather chemist to know. The book is based upon the "Text-book of Tanning," written by the author, the practical parts of which have been considerably extended for the purpose. Only thoroughly satisfactory methods which are known to fulfil the most stringent requirements as to accuracy and rapidity are given, and they are explained in detail. The applications of the microscope to leather chemistry are well treated, and a chapter is devoted to a sketch of general methods of bateriology, with references to manuals which deal with the subject more fully. Although the reader is assumed to have a knowledge of the elements of leather manufacture and chemical theory, the book is one which will be suitable for the use of the technical student from the beginning of his course, and the chemist engaged in the leather industries will also find that it contains all the information he wants for the ordinary routine work which falls to his lot, and also that it gives him much help in attacking the more difficult problems demanding originality and ingenuity with which he is frequently confronted.

The Paper Makers' Directory of all Nations. Seventeenth Edition. London: Dean and Son, Limited. 1908.

THE new edition of this Directory, which has been much appreciated by all who are interested in any of the branches of the Paper trade, is somewhat larger than its predecessors, the additional matter including a short summary of the recognised customs of the trade relating to paper making in Britain, and a table of the sizes of British papers. In the lists the addresses of paper makers are classified according to various systems and are well arranged, and the Index to Commercial Prospectuses greatly simplifies reference to the many advertisements which the book contains.

MISCELLANEOUS.

Impersonation.—Consulting and analytical chemists and others are warned against receiving a tall seedy-looking man, who, on the plea of ill-health, solicits pecuniary assistance by impersonating a certain Fellow of the Institute of Chemistry in practice at Warrington.

British Association for the Advancement of Science.—The following were the Officers and Committee of Section B (Chemistry) at the Dublin Meeting of the British Association:—

President—Prof. F. S. Kipping, D.Sc., Ph.D., F.R.S.

Vice-Presidents—Sir Charles A. Cameron, M.D.; Prof. A. Smithells, B.Sc., F.R.S.; Prof. W. Noel Hartley, D.Sc., F.R.S.; Prof. Sydney Young, D.Sc., F.R.S.

Secretaries—E. F. Armstrong, D.Sc., Ph.D. (Recorder); Alex. McKenzie, M.A., D.Sc., Ph.D.; F. M. Perkin, Ph.D.; James H. Pollock, D.Sc.

Committee—Dr. W. E. Adeney; Prof. H. E. Armstrong, F.R.S.; Dr. G. H. Bailey; J. L. Baker; W. Barlow, F.R.S.; Dr. G. T. Beilby, F.R.S.; Prof. A. Brown; Dr. F. D. Chattaway, F.R.S.; H. F. Coward; H. Crompton; Sir J. Dewar, F.R.S.; Prof. A. E. Dixon; Prof. H. B. Dixon, F.R.S.; Prof. E. Divers, F.R.S.; Prof. Donnan; Prof. W. Dunstan, F.R.S.; T. Fairley; Dr. A. Findlay; Dr. L. F. Guttmann; A. D. Hall; Prof. A. G. Vernon Harcourt, F.R.S.; Dr. A. Harden; Prof. G. G. Henderson; Dr. A. Lapworth; Dr. T. M. Lowry; Dr. J. E. Mackenzie; W. MacNab; Dr. H. Marshall, F.R.S.; Dr. H. McCombie; Dr. A. Meldrum; J. H. Millar; J. O'Farelly; Prof. K. J. P. Orton; Prof. W. H. Perkin, F.R.S.; Dr. R. H. Pickard; Prof. W. J. Pope, F.R.S.; H. Ramage; Sir W. Ramsay, K.C.B., F.R.S.; R. Robinson; Prof. H. Ryan; Dr. H. J. S. Sand; Prof. A. Senier; J. L. Simonsen; Dr. A. Slator; Dr. Ida Smedley; John Smythe; Prof. J. J. Sudborough; Miss B. Thomas; Dr. J. F. Thorpe, F.R.S.; Prof. T. Turner; Dr. A. E. H. Tutton, F.R.S.; Dr. A. J. Walker; A. F. Watson; Dr. C. Weizmann; Prof. E. Werner; Dr. N. T. M. Wilsmore; Dr. M. A. Whiteley; Dr. G. Young.

The Papers brought before the Section were as follows:—

Presidential Address by Prof. F. S. KIPPING, D.Sc., F.R.S.

Prof. W. H. PERKIN, F.R.S.—Synthetical Experiments in the Terpene Series.

C. WEIZMANN—Preparation of Camphor from Oil of Turpentine.

R. ROBINSON—Brazilin and Haematoxylin.

Prof. W. J. POPE, F.R.S., and JOHN READ—The Dynamic Isomerism of Oxymethylene Camphor Derivatives.

J. A. SMYTHE—Benzyl Sulphoxide, a possible example of tautomerism.

Dr. F. D. CHATTAWAY, F.R.S.—(*a*) Action of Halogens upon Aromatic Hydrazines. (*b*) Some Reactions of Dichloro-urea.

Prof. F. S. KIPPING, F.R.S.—Optically active Silicon Compounds.

Report of the Committee on Dynamic Isomerism.

Discussion on "Nature of Chemical Change," opened by Prof. H. E. ARMSTRONG, F.R.S.

Dr. LUDWIG MOND, Dr. H. HIRTZ, Mr. D. COWAP—Note on a Volatile Compound of Cobalt with Carbon Monoxide. Communicated by Sir J. DEWAR, F.R.S.

Prof. W. J. POPE, F.R.S., and WILLIAM BARLOW, F.R.S. The Structure of the Open Chain Hydrocarbons.

H. BATEMAN—Dynamics of Chemical Action and the meaning of Valency.

Prof. H. R. PROCTOR—Report on Colloids.

Dr. A. FINDLAY—The Influence of Colloids on the Absorption of Carbon Dioxide by Water.

Dr. J. TIMMERMANS—Densities of Liquids at Low Temperatures.

Dr. A. MELDRUM—The Work of Two Irish Chemists—Bryan Higgins and William Higgins.

JULIAN L. BAKER and H. F. E. HULTON—Action of the Enzymes of Malt on Ungerminated Cereals.

JULIAN L. BAKER and F. E. DAY—Preparation of Pure Maltose.

Discussion on "Gaseous Explosions," in Joint Meeting with Sections A and G.

Sir WILLIAM RAMSAY, K.C.B., F.R.S.—The Inactive Gases.

Prof. W. N. HARTLEY, F.R.S.—Lithium in Radio-active Minerals.

Dr. KAMERLINGH ONNES—The Liquefaction of Helium. Communicated by Sir JAMES DEWAR, F.R.S.

Sir JAMES DEWAR—Anticipations and Experiments on the Liquefaction of Helium.

Prof. H. E. ARMSTRONG, F.R.S.—(*a*) The Curriculum in Chemistry. (*b*) The Properties of Oxygen.

Dr. H. J. S. SAND—Demonstration on the Rapid Electro-analytical Separation of Metals.

W. E. HUGHES and Dr. F. M. PERKIN—Studies on the Electro-deposition of Metals.

Dr. J. HÜBNER—Mercerisation in Cotton.

Prof. T. TURNER—Transparent Silver and other Thin Metallic Films.

Report of the Committee on Wave Lengths.
Discussion on "Problems of Fermentation," by Dr. A. Harden, Prof. Adrian Brown, Dr. A. Slator, Dr. E. F. Armstrong, and others.
Prof. Adrian Brown—The Selective Permeability of certain Seeds.
Discussion on Peat, by Dr. Woltereck, Capt. Sankey, Profs. Ryan, Johnson, and Lyon, Dr. Adeney, Mr. K. B. Eller, and others.
Reports of Committees—
1. Hydroaromatic Substances. 2. Aromatic Nitramines. 3. Isomorphous Benzene Derivatives.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Atacamite in Copper Ores.—Could any reader give me some information about the following:—The copper existing as atacamite in copper ores sent to Swansea is deducted from the total copper content. In the reports I have seen, the chlorine is given, but not the corresponding amount of atacamite. As I have come across many ores containing NaCl mixed with carbonates, silicates, &c., of copper, but no atacamite, I am anxious to know whether salt in any other chloride is also charged up as atacamite and the deduction made. If anyone could give me the methods of assay for chlorine employed in atacamite and other copper ores, and tell me how the whole thing is arranged, I should be obliged.—T. C. W.

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Town Hall, Old Street, E.C.,
September 6th, 1908.

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SOUTH-WESTERN POLYTECHNIC INSTITUTE,
MANRESA ROAD, CHELSEA, S.W.

EVENING CLASSES commence SEPT. 21st.
DAY COLLEGE COURSES commence SEPT. 28th.

Department of Chemistry & Metallurgy.

Head of Department—J. B COLEMAN, A.R.C.S., F.I.C.

PHYSICAL CHEMISTRY.—A Course of about thirty-six Experimental Lectures on this subject, suitable for University Students, will be given by Mr. J. C. Crocker, M.A., D.Sc. Suitable Practical Work will be taken on the same day.

Syllabus.—Determination of Molecular Weights, Constitution and Physical Properties; Solution; Alloys; Solubility; Association and Dissociation; Electro-chemistry; Thermo-chemistry; Chemical Equilibrium; Velocity of Reaction.

Day Course.—Fridays: Lecture, 2 to 3; Practical, 3 to 5. Fee, 21s. per Term.

Evening Course.—Fridays: Lecture, 7 to 8; Practical, 8 to 10. Fee, 10s. per Session.

METALLURGY.—Elementary and Advanced Courses on Metallurgy are given, at the times stated below, by Mr. W. E. Oakden, F.C.S.

The Metallurgical Laboratory is fully equipped for Wet and Dry Assays. It is provided with the latest apparatus for experimental work in Metallography, Pyrometry, and Electrical Furnace Work. Students may now carry out the work for the B.Sc. Degree in the Faculty of Engineering (Metallurgy).

Day Courses.—Elementary—Tuesdays: Lecture, 4 to 5; Practical, 2 to 4. Fee, 21s. per term.
Advanced—Wednesdays: Lecture, 4 to 5; Practical, 2 to 4. Fee, 21s. per Term.

Evening Courses. Elementary—Tuesdays: Lecture, 7.30 to 8.30; Practical, 8.30 to 10. Fee, 10s. per Session.
Advanced—Wednesdays: Lecture, 7.30 to 8.30; Practical, 8.30 to 10. Fee, 10s. per Session.

Day Laboratory Work can be taken at other times by arrangement.

SIDNEY SKINNER, M.A., Principal.

THE CHEMICAL NEWS.
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(STUDENTS' NUMBER).

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

Candidates for any Degree in this University must either have passed the Matriculation Examination in this University, or be admitted under the Statute which provides that the Senate may admit graduates of or persons who have passed the examinations required for a degree in other Universities approved by it. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, &c., are open to Women upon exactly the same conditions as to Men.

There are three Examinations for Matriculation in each year; commencing on the second Monday in September, January, and June (or July, as may hereafter be determined).

Every candidate entering for the Matriculation Examination must pay a Fee of £2. If a candidate withdraws his name, or fails to present himself at the Examination, or fails to pass it, the Fee shall not be returned to him.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following five subjects:—(1) English—Composition, Précis Writing, salient facts in English History and Geography. (2) Elementary Mathematics. (3) Latin or Elementary Mechanics, or Elementary Physics—Heat, Light, and Sound, or Elementary Chemistry, or Elementary Botany. (4) and (5) Two of the following subjects, neither of which has already been taken under Section (3). If Latin be not taken, one of the other subjects selected must be another Language from the List, either ancient or modern: — Latin, Greek, French, German, *Arabic, *Sanskrit, *Spanish, *Portuguese, *Italian, *Hebrew, and *Zoology, Ancient History, Modern History, Logic, Physical and General Geography, Geometrical and Mechanical Drawing, Mathematics (more advanced), Elementary Mechanics, Elementary Chemistry, Elementary Physics—Heat, Light, and Sound, Elementary Physics—Electricity and Magnetism, and Botany. Candidates in subjects marked with asterisk must give at least two months' notice before the commencement of the Examination.

A Pass Certificate, signed by the Principal, will be delivered to each successful candidate after the Report of the Examiners has been approved by the Senate.

Several valuable Scholarships and Exhibitions are available to students.

Intermediate Examination in Science.

The Intermediate Examination in Science will commence on the second Monday in July.

No candidate is admitted to this Examination unless he has passed, or been admitted under the Statute referred to above as exempt from, a Matriculation Examination not later than that of the preceding January.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. This Examination will consist of two printed papers and a practical examination.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. Examination.

The B.Sc. Examination will be held on the fourth Monday in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously, and to have passed the Matriculation Examination at least three years previously.

The Fee for this Examination is £5.

Examination for Honours.

For the examination for Honours in Chemistry candidates are required to show a general acquaintance with General Theoretical Chemistry, Chemistry of Carbon Compounds, Physical Chemistry, and History of Chemistry since the time of Boyle.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

Doctor of Science.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

Preliminary Scientific (M.B.) Examination.

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the second Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

The Fee for this examination is Five Pounds.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. Odling, F.R.S.

Lees Reader in Chemistry—H. Brereton Baker, M.A., D.Sc., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities and other persons suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, M.A., J. Watts, M.A., and J. E. Marsh, M.A., F.R.S., N. V. Sidgwick, M.A., A. F. Walden, M.A., B. Lambert, B.A.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

There are also laboratories which specialise in different parts of the subject:—*Physical Chemistry*, Balliol and Trinity College Laboratory: D. H. Nagel, M.A., H. B. Hartley, M.A. *Inorganic Chemistry*, Christ Church Laboratory: Dr. Baker. *Quantitative Analysis*, Magdalen College Laboratory: J. J. Manley, M.A. Jesus College Laboratory: D. L. Chapman, M.A. Queen's College Laboratory: Rev. H. B. Cronshaw, M.A.

Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—W. J. Pope, F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy—Sir James Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in any term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

A graduate of another University may be admitted as an "advanced" student, and obtain a degree after two years' residence in the University.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science at the several Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instruction. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrary, Cambridge, or from the *Cambridge University Calendar*.

UNIVERSITY OF DUBLIN.

TRINITY COLLEGE.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.

Professor of Applied Chemistry—Emil A. Werner, F.C.S., F.I.C.

Demonstrator—W. C. Ramsden, F.C S.

Junior Demonstrators—W. R. G. Atkins, B.A., T. A. Wallace.

The general Quantitative and Research Laboratories include working accommodation for about 130 Students. The Laboratories will open on October 1st. Lectures will commence about November 1st.

The Laboratories and the Lectures ofthe Professor of Chemistry can be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The Lectures delivered are:—

1. *Inorganic Chemistry and Chemical Philosophy.*—Elementary, first year; Advanced Inorganic Chemistry, second year; Physical Chemistry, third year.
2. *Organic Chemistry.*—General, second year; advanced, third year.
3. *Metallurgy.*—A Course for Engineering and Technical Students.
4. *Agricultural Chemistry.*—Theoretical and Practical Courses.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of Practical Chemistry for Medical Students begins early in April and terminates about the end of June.

A special course for Dental Students will be given.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

By recent decrees, Prizes in Chemistry and Physics will be given in future at the October (Arts) Entrance Examination, and also at the Terminal Examinations of the Junior and Senior Freshmen Years.

Similarly, two Science Scholarships will be obtainable by Undergraduates, and tenable for five years. These Foundation Scholars receive £20 per annum, have free commons, their chambers for half the charge paid by other students, and their tutorial fees are at one-fourth the usual rates.

KING'S COLLEGE.

Senior Professor of Chemistry—J. M. Thomson, LL.D., F.R.S.

Professor—Herbert Jackson, F.C.S.

Lecturer and Demonstrators—P. H. Kirkaldy, F.C.S., H. L. Smith, B.Sc., S. W. Collins, B.Sc., and L. Hinkel.

The Academical Year consists of Three terms. The days fixed for the commencement of Terms in 1908-1909 are Sept. 30, Jan. 6, and April 28.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated. Examinations of the Class, both *vivâ voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Chemical Analysis, both by liquid tests and the blowpipe, analysis of ores, liquids, &c., and Elementary Volumetric Analysis.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Fees.—Chemistry: Winter Session, £5 5s.; Summer Session, £3 3s. Practical Chemistry: Winter Session, £8 8s.; Summer Session, £4 4s. Experimental and Analytical Chemistry—Five days a week: One month, £4 4s.; One Term, £10 10s.; Two Terms, £18 18s.; Three Terms, £26 5s. Three days a week: One month, £2 12s. 6d.; One Term, £6 6s.; Two Terms, £11 11s.; Three Terms, £15 15s.

For fuller details the separate Syllabuses provided for each class should be consulted.

METALLURGY.

Professor—A. K. Huntington, A.R.S.M, F.I.C., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is paid to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery.

Fee, £3 3s. for the Course.

PHOTOGRAPHY.

Lecturer—Prof. J. M. Thomson, LL.D., F.R.S.

For particulars apply to Prof. Thomson.

EVENING CLASSES.

Classes for Evening Instruction in various subjects are held during the Winter Session.

UNIVERSITY COLLEGE.

FACULTY OF SCIENCE.

Professors—Sir William Ramsay, K.C.B., LL.D., F.R.S. (Inorganic and Physical Chemistry); J. Norman Collie, Ph.D., F.R.S. (Organic Chemistry).

Assistants—E. C. C. Baly, F.I.C.; S. Smiles, D.Sc.; N. T. M. Wilsmore, M.Sc.; Katharine A. Burke, B.Sc.; R. W. Gray, Ph.D.; and W. B. Tuck, B.Sc.

The Session is divided into three Terms, as follows:—First Term, from October 5 to December 18; Second Term, from January 12 to March 31; Third Term, from April 27 to July 7.

Introductory Course of Inorganic Chemistry.

Tuesday and Thursday, at 9. Practical, Thursday, 2 to 3.30, or 3 30 to 5. Fee, £10 10s.

This Course treats of the chief physical and chemical characters of the Non-metallic Elements, their preparation and characteristic tests.

Junior Course of Inorganic Chemistry.

First and Second Terms: The Class meets four times a week, on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

In this Course the physical principles bearing on Chemistry are first discussed, and the Chemistry of the Elements and their compounds is treated in considerable detail, under the headings—Elements; hydrides, halides, oxides, sulphides, &c., borides, carbides and silicides, nitrides, phosphides, &c., and alloys. Special attention is devoted to substances of commercial importance. The concluding Lectures are devoted to Physical Methods and their bearing on Chemical Problems.

Third Term: Lectures will be given on Mondays and Fridays at 9 and on Wednesdays at 11, on the chief types of Carbon Compounds.

Fees: Course, £7 7s.; First or Second Terms, £4 4s.

A Practical Class will meet throughout the Session.

Course of Physical Chemistry.

October to February: Tuesday and Thursday at 9. February to June: Monday and Saturday at 9.

The Principles of Chemistry will be specially considered, comprising the Atomic Theory, Chemical Classification, the Periodic Law, Thermal Chemistry, Dissociation, the Application of Physical Methods to the Solution of Chemical Problems, and the influence of Mass and Temperature on the progress of Reactions. Special attention is paid to the most recent Chemical Theory researches.

Fees:—Courses, £5 5s.; Term, £2 2s.; for a second course, £1 1s.

Senior Course of Inorganic Chemistry.

This Course will begin about the middle of February; Tuesday and Thursday at 9. Fee, £3 3s.

Organic Chemistry.

Mon. at 12, Wed. and Fri. at 9, during the session.

This Course is suitable for Students who intend to study Chemistry from a scientific standpoint. No previous knowledge of Organic Chemistry is expected of those attending the Class, which should, however, be taken concurrently with the Course of Physical Chemistry, and with Practical Organic Chemistry in the Laboratory.

Fee:—For the Course, £6 6s.; for a Term, £2 12s. 6d.; for a Second Course, £3 3s.

An Advanced Course will be held twice a week throughout the Session for those engaged in prosecuting research in Organic Chemistry. Fee, £5 5s.; Term, £2 2s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Laboratories of General and of Organic Chemistry.

The Laboratories are open daily from 9 a.m. to 5 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Courses qualify Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. Several valuable Scholarships are available to students.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY.

Professor of Chemistry—W. A. Tilden, D.Sc., F.R.S.

Assistant Professors—M. O. Forster, Ph.D., D.Sc., F.R.S.; G. T. Morgan, D.Sc., A.R.C.S.; J. C. Philip, M.A., Ph D, B.Sc.

The Imperial College of Science and Technology, incorporated under the Royal Charter of July 8, 1907, is an institution or group of associated colleges with its principal seat at South Kensington.

The purposes of the Imperial College are to give the highest specialised instruction, and to provide the fullest equipment for the most advanced training and research in various branches of science, especially in its application to industry; and to do all and any of such things as the Governing Body consider conducive or incidental thereto, having regard to the provision for those purposes which already exists elsewhere.

For these purposes, the Governing Body, subject to the provisions of the Charter, are to carry on the work of the Royal College of Science, and the Royal School of Mines, and may establish Colleges and other Institutions or Departments of Instruction. Any Institution or Department so established, and, subject to the conditions of the Charter, the Central Technical College of the City and Guilds of London Institute, are to be integral parts of the Imperial College; and the Central Technical College is to be called and known in future as the City and Guilds College.

Subject to agreement with the authorities of any College or other Institution, the Governing Body may by resolution recognise that College or Institution or any Department thereof, as being in association with the Imperial College for all or any of the purposes of the Charter, but no such resolution is to be valid or operative until allowed by the King in Council.

The Charter further provides that the Imperial College shall be established in the first instance as a School of the University of London. Students of the Imperial College who have matriculated at the University of London may therefore proceed to the Science degree of the University as "Internal Students."

The Session 1908-9 will see certain modifications of the work as carried on hitherto by the constituent Colleges, and while intending students can rely generally on the carrying out of the scheme as outlined, it must be understood that it may be subject to modification in detail.

Attention is particularly directed to the conditions of admission and to the extended facilities for Research Work.

The ordinary courses of instruction are planned so as to extend over four years instead of three years, as heretofore, in the several constituent Colleges. They are generally similar for all students during the first year, and to a less extent during the second year, after which they are specialised according to the particular course which the student is taking.

The following Diplomas have been awarded in the past to Students of the several constituent Colleges:—

The Associateship of the Royal College of Science (A.R.C.S.) in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, Geology.

The Associateship of the Royal School of Mines (A.R.S.M) in one or more of the following divisions:—Metallurgy, Mining.

The Associateship of the City and Guilds Institute (A.C.G.I.) in one or more of the following divisions:—Chemistry, Engineering (Civil and Mechanical), Engineering (Electrical).

The instruction in Chemical Science embraces:—

1. Courses of lectures on the laws and general principles of Chemistry, including the special study of compounds of carbon, usually called "Organic Chemistry"; on the theory and methods of Chemical Analysis; and on Physical Chemistry.

2. A systematic Laboratory course for the practice of Qualitative and Quantitative Analysis.

An examination will be held at the end of each course of instruction, and all candidates for a Diploma in Chemistry will be required to qualify in each successive stage.

A Laboratory course is provided for advanced students desirous of acquiring a knowledge of the methods employed in research and for the prosecution of Chemical Investigations.

Full details can be obtained from the College Calendar, published by Eyre and Spottiswoode (or through any bookseller), price 6d.

THE SCHOOL OF PHARMACY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The Sixty-sixth Session will commence on Sept. 30, 1908.

Professors—Chemistry, Arthur W. Crossley, D.Sc., Ph.D., F.I.C., F.R.S., (Dean); Pharmaceutics, Henry G. Greenish, F.I.C., F.L.S.

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also of those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the Conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies. Certificates of attendance at the Course of Pharmacy is also accepted by the Conjoint Board.

Prospectuses and further information may be obtained from the Dean of the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

University of Wales.

Director of the Edward Davies Chemical Laboratories and Professor—J. J. Sudborough, D.Sc. (Lond.), Ph D. (Heidelberg), F.I.C.

Assistant Lecturers and Demonstrators—A. Brooke, Ph.D. (Strass.), and T. C. James, M.A. (Cantab.), B.Sc.

Lecturer in Agricultural Chemistry—J. Jones Griffith, B.Sc. (Wales).

The College is open to men and women students above the age of sixteen years. The Session commences on Sept. 29th, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Intermediate Science Course; four lectures weekly throughout the Session. (2 and 3) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, three lectures weekly on General and Physical Chemistry. (Courses A and B will generally be given in alternate Sessions; for 1908-1909, Course B). (4 and 5) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratories are open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays. Regular Courses of practical work, suitable for the B.Sc. degree of the Universities of London and Wales, or for the Associateship of the Institute of Chemistry, can be followed. Facilities are given for Students wishing to undertake research work. Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 12s. 6d. per term, and for twelve hours, 25s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 15, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A Constituent College of the University of Wales.

Chemistry.—Professor, K. J. P. Orton, M.A., Ph.D., F.I.C. Assistant Lecturer and Demonstrator, Alice E. Smith, B.Sc. Assistant Lecturer in Agricultural Chemistry, R Grunt, Ph.D., B.Sc. Junior Demonstrator, J. O. Hughes, B Sc.

Physics.—Professor, E. Taylor Jones, D.Sc. Assistant Lecturers and Demonstrators, A. H. Verguson, B.Sc., and W. E. Williams, B.Sc.

The Session opens September 29th, 1909. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £3 13s. 6d.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 3s. Advanced Lectures on Organic Chemistry, £1 1s.

Agricultural Chemistry.—Fee, £2 2s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 5 p.m. for instruction in Chemical operations and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s. Composition Fee for all Laboratory Classes of the Intermediate Science Course taken in one year, £4 4s.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and by the Conjoint Boards of the Royal Colleges of Surgeons and Physicians, and students can make one *Annus medicus* at the college. Students are prepared for the First Examination of the Universities mentioned, and of Conjoint Board of the

Royal Colleges of Surgeons and Physicians. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.
Assistant Professor—E. P. Perman, D.Sc., F.C.S.
Demonstrator—R. D. Abell, D.Sc.
Lecturer in Metallurgy—A. A. Read, F.I.C., F.C.S.

The Session commences October 6th, and terminates on June 15th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 50 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s.

The Intermediate Course consists of about 80 lectures held during the Lent and Summer terms in continuation of the Junior Course; together with laboratory practice it forms the qualifying course for the Intermediate Examination of the University of Wales, and will cover the subjects required for the Intermediate Examination in Science (Part I.) of the University of London. Fee, £4 4s.

The Senior Course consists of about 80 lectures on Inorganic Chemistry; Fee, £3 3s.

The following lectures on Metallurgy will be given by Mr. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held, and practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £2 2s. per term; twelve hours, £3 3s. per term; eighteen or more hours, £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students wishing to graduate at a Scottish University, or preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in September, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry—Francis Francis, D.Sc., Ph.D., F.I.C.
Lecturer (Physical Chemistry)—James W. McBain M.A.
Lecturer—Oliver C. M. Davis, B.Sc., F.I.C.
Lecture Assistant—J. H. Sturgess.

The session 1907-1908 will begin on October 1. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. A Laboratory has recently been fitted with a complete equipment for all ordinary measurements in Physical Chemistry. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the College. Several Scholarships are tenable at the College. Full information may be obtained from the Registrar.

Day Lectures.

Inorganic Chemistry.

The Courses treat of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Introductory Course.—Three Lectures a week will be given during the First and Second Terms, and at least one Lecture a week during the Third Term. Fee, £3 13s. 6d.

General Course.—Three Lectures a week will be given throughout the Session. Fee, £3 13s. 6d.

Systematic Physical Chemistry (a course extending over two Sessions).—Two Lectures a week will be delivered throughout the Session. Fee, £3 13s. 6d.

Electro-chemistry.—One Lecture a week will be given during the Third Term. Fee, £1 1s.

Advanced Course.—Two Lectures a week will be given throughout the Session. Fee, £3 13s. 6d.

Organic Chemistry.

General Course—Three Lectures a week will be given throughout the Session. Fee, £3 13s. 6d. An advanced course of lectures will also be given one day a week during the session. Fee, £2 2s.

Colloquium.

A weekly Colloquium will be held by members of the Staff to discuss recent advances in the various departments of Chemistry. Students and others interested are invited to attend.

Practical Chemistry.—Laboratory Instruction.

The Chemical and Metallurgical Laboratories will be open daily from 9 a.m. to 5 p.m., except on Saturdays, when they are open to senior students only. Instruction will be given in the Laboratory in all branches of Inorganic, Organic, and Physical Chemistry. Special facilities will be afforded to those who desire to carry out research or to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures. Fees in Guineas—

Days per Week ..	Five.	Four.	Three.	Two	One.
Per Session	15	12½	10	7½	5
,, Two Terms ..	11	9	7½	5½	3½
,, One Term ..	7	6	4½	3½	2½

Students may arrange to divide their days of laboratory work into half-days. Special facilities are offered for Research and Post-graduate work.

Chemical Scholarship.—Among others, a Chemical and a Metallurgical Scholarship each of £25 are offered for competition.

Evening Lectures.

A course of Lectures dealing with the principles and theories of modern Chemistry will be delivered during the First and Second Terms. Fee, 10s. 6d.

Practical Chemistry — Laboratory Instruction. — The Laboratory will be open one evening a week from 6 till 9. Instruction will be given in Qualitative and Quantitative Analysis, and in the Preparation of Chemical Products Fees:—Two Terms, 21s; One Term, 12s. 6d.

University College, Bristol, has been approved by the Council of the Institute of Chemistry as a College at which all the subjects required for the admission of Associates to the Institute are taught.

The Calendar of the College, price 1s. (post-free, 1s. 4d.), containing detailed information of the various Courses, may be obtained on application to the Registrar.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL.

Chemistry.

Professor—J. Wertheimer, B.Sc., B.A., F.I.C., F.C.S.

Assistant Professor—Frederick W. Rixon, M.Sc., Ph.D.

Lecturers—H. A. M. Borland, A.R.C.S.; E. E. Elt, B.Sc

Demonstrators—E. H. T. Parker; D. A. Baker.

Assistants in Chemical Laboratory—W. F. Phillips and C. Cox.

The Laboratories of this Department are open during the Term on every week-day as a School of Practical Chemistry and Analysis to Students of either sex. Each Student works independently, and receives individual instruction and help.

The training in this Department is intended to fit Students to become Professional Chemists, to prepare them for Medical or Pharmaceutical examinations in Chemistry, to instruct them in the branches of Applied Chemistry required in Manufactures and Agriculture.

Special facilities will be given to Students wishing to undertake research work approved by the Professor; and the Courses provide for the Examinations in Chemistry for the B.Sc., M.B., and D.Sc. degrees of the University of London.

The three years' course at this College in the subjects of Theoretical and Practical Chemistry, Theoretical and Practical Physics, and Elementary Mathematics, is accepted by the Council of the Institute of Chemistry as satisfactory evidence of the training of candidates for the Associateship of the Institute.

The Laboratories are open every week-day from 9.30 till 12.30, and from 2 to 5 p.m., except Saturday, when they close at 12 30.

The Annual Fee of £10 10s. secures (in addition to the use of the Laboratory) permission to attend the Lectures in Physics and Mathematics as well as Chemistry, and to use the Physical Laboratory and Engineering Workshop.

The College Day Classes re-open on Sept. 15, and the Evening Classes commence on Monday, September 28.

Further detailed information may be obtained from the College Calendar, price 6d., or the Prospectus for Day or Evening Classes (free).

UNIVERSITY OF BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., M.Sc., LL.D., F.R.S., P.I.C.

Assistant Lecturers and Demonstrators—Alex. Findlay, M.A., D.Sc., Ph.D.; Hamilton McCombie, M.A , Ph.D., B.Sc., A.R C.S., A I.C.; C. K. Tinkler, D.Sc., and T. J. Murray, Ph D., M.Sc.

The Session will be opened on October 1st, 1908.

Lecture Courses.

First Year.—A. This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Four hours weekly during the Winter and Spring terms. Mondays to Thursdays inclusive, at 9.30 to 10 30 a m. Fee, £5 5s. B. This part of the course includes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9.30 to 10 30 a.m. Fee, £1 11s. 6d.

Second Year. — Advanced Organic Chemistry.— This course extends over two years, and is divided into two parts:—(*a*) Carbon Compounds of the Fatty Series; (*b*) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. *General and Physical Chemistry.*— This course will deal in outline with the more recent developments of Theoretical Chemistry. The class meets once weekly by arrangement during the three terms. Fee, £1 11s. 6d.

Third Year.—A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. A further Course on General and Physical Chemistry, in which special subjects attracting attention at the time receive treatment. Fee, £1 11s. 6d.

Practical Chemistry.

The instruction in Practical Chemistry extends over three years. The Laboratory will be open daily from 9.30 to 5, except Saturdays, when it closes at 1 p.m. Fees—

	All day.	Three hours per day.	Three hours per day; five days a week.	Three hours per day; three days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term ..	7	4½	4	2½
Two Terms .	13	8½	7½	5
Three Terms	18	12	11	6¼

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Special facilities are given to Advanced Students for the prosecution of original research.

Metallurgy.

There is a separate University department for Metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in June.

Ascough Scholarship.—One Open Scholarship of the value of about £30 is awarded annually in July.

Bowen Scholarship.—One Open Scholarship in Metallurgy, value about £96, is awarded annually in June.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

CITY OF BRADFORD TECHNICAL COLLEGE.

Principal—Prof. W. M. Gardner, M.Sc.

Department of Chemistry and Dyeing.

Professor of Chemistry and Dyeing—W. M. Gardner, M.Sc.

Assistant Professor of Chemistry—B. North, A.R.C.Sc. (Lond).

Lecturers in Chemistry—L. L. Lloyd, Ph.D.; H. H. Hodgson, M A., B Sc., Ph.D.; S. F. Stell, F.C.S.

Demonstrators in Chemistry—A. E. Findley, B.Sc.; S. M. Sutcliffe, F.C.S.

Lecturer in Physics—J. A. Tomkins, A.R.C.Sc. (Lond.).

Demonstrator in Physics—E. B. Walker.

Lecturer in Dyeing—A. B. Knaggs, F.C.S.

Demonstrator in Dyeing—T. Brooke.

Lecturer in Gas Manufacture—W. Cranfield.

Lecturer in Botany, Biology, and Pharmacy—W. West, F.L.S., Ex. Pres. Yorkshire Naturalists' Union.

The following courses of instruction are provided:—

I. *General Chemistry Course*, extending over four years, including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Electro-chemistry, Physical Chemistry, Crystallography, Fuels, Lighting and Ventilation, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry, Physics, Bacteriology, and Microscopy.

II. *Chemistry and Dyeing*, extending over four years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c.

III. *Chemical Engineering*. Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. *Sanitary Science*. One year's Course, recognised by the Sanitary Institute as preparing for their certificate examination. Subjects: Chemistry, Physics, Sanitary Engineering, Sanitary Law, Building Construction, Drawing, Physiology, and Bacteriology.

V. *Dyeing*. Extending over one or two years.

VI. *Textile and Dyeing*. Arranged for those Students who desire to study the two subjects simultaneously.

VII. *First Professional Examination, Conjoint Medical Board (M.R.C.S., L.R.C.P.), London*.—Attendance at the College and College Certificates in Chemistry, Physics, and Biology are recognised by the Conjoint Board for Medical Studies as a qualifying curriculum.

VIII. *General Pharmaceutical Course*. Prepares for the Minor and Major Pharmaceutical Examinations. Each extends over two years on four half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

Chemical Department.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Assistant—W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of minera' bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

THE UNIVERSITY OF LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc., F.R.S.

Professor of Organic Chemistry—Julius B. Cohen, Ph.D, B.Sc.

Lecturer on Physical Chemistry—H. M. Dawson, D.Sc, Ph.D.

Assistant Lecturers and Demonstrators—W. H. Perkins, B.Sc.; W. Lowson, B.Sc., F.I.C.

Demonstrators—H. Calam, M.Sc.; A. T. King, B.Sc; J. Marshall, B.Sc.

The Session begins October 1, 1908.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £4 4s.

1a.—Supplementary Course of Inorganic and Organic Chemistry. Fee, £3 13s. 6d.

2. Advanced Inorganic Chemistry.—Metals. Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £3 13s. 6d.

3. Advanced Inorganic Chemistry.—Non-metals. Tuesday, Thursday, and Saturday, at 9.30 a.m. Fee, £3 13s. 6d.

4. Organic Chemistry.—Tuesday, Thursday, and Saturday at 12 noon Fee £3 13s. 6d.

5. Honours Courses—(*a*) Organic Chemistry: Monday, Wednesday, and Friday at 12 noon in the First and Second Terms; fee, £2 12s. 6d. (*b*) History of Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the First Term; fee, £1 11s. 6d. (*c*) Physical Chemistry: Monday, Wednesday, and Friday at 9 30 a.m. in the Second and Third Terms; fee, £2 12s. 6d. (*d*) Electro-chemistry: One hour weekly; 31s. 6d.

6. Chemistry of Food and Drugs—Special class for Students taking Final Examination of the Institute of Chemistry in Branch E (Food and Drugs). £2 2s.

Laboratory Courses.

The University Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—Students working six days per week, £21; five, £18 18s.; four, £16 16s.; three, £13 13s.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 from April to June. Fee, £5 5s.

Tinctorial Chemistry and Dyeing Department.

Professor—Arthur G. Green, M.Sc., F.I.C.

Lecturer and Research Chemist—A. G. Perkin, F.R.S., F.I.C.

Assistant Lecturer—Ian Q. Orchardson, B.Sc.

Demonstrator—G. H. Frank, B Sc.

The Courses extend over periods of three or four years, and are intended for those who wish to obtain a full scientific and practical education in the art of dyeing, colour manufacture, &c. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, *e.g.*, the sons of manufacturers, calico printers, managers, master dyers, &c., or in the manufacture of coal-tar products and dyestuffs.

Leather Industries Department.

Professor—H. R. Procter, M.Sc., F.I.C.

Assistant Lecturer and Demonstrator—H. G. Bennett, M.Sc.

Demonstrator—Harold Brumwell.

Research Assistant—D. J. Law, B.Sc., A.I.C.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—R. S. Seton, B.Sc.

Lecturer in Agricultural Chemistry—C. Crowther, M.A., Ph.D.

The full Course occupies three years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out door agriculture at the University Farm.

Fuel and Metallurgical Department.

Professor—William A. Bone, D.Sc., Ph.D, F.R.S.

The Courses extend over two, three, or four years, and are suitable for those who are preparing for posts either as Gas Engineers or in Fuel and Metallurgical industries.

The Courses in Gas Engineering and the Technology of Fuel will chiefly deal with the manufacture and distribution of coal-gas and gas-lighting problems, by product coking processes, and the production and application of gaseous fuels for heating and power purposes.

The Metallurgical Courses, besides dealing with general processes for the concentration and extraction of ores, will be chiefly directed to problems underlying blast furnace and open-hearth steel practice, and to the microstructure, physical properties, and heat treatment of steel and other industrial alloys.

Research Students are admitted to the University Laboratories on reduced terms.

Several valuable Fellowships and Scholarships are at the disposal of the University, including a Fellowship of £100 offered by the Institution of Gas Engineers, and the Salt, Akroyd, Brown, Baines, Emsley, Craven, Leeds City Council, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The North, East, and West Ridings County Council's Scholarships are tenable at the University of Leeds.

UNIVERSITY OF LIVERPOOL.

Professor of Chemistry—J. Campbell Brown, D.Sc.

Professor of Physical Chemistry—F. G. Donnan, M.A. Ph.D.

Lecturer on Organic Chemistry—A. W. Titherley, D.Sc., Ph.D.

Lecturer on Metallurgy — Guy D. Bengough, M.A., A.R.S.M.

Demonstrators and Assistant Lecturers — A. T. de Mouilpied, M.Sc., Ph.D.; H. Bassett, B.Sc., Ph.D., D.es.Sc.; F. J. Brislee, D.Sc.; A. Rule, M.Sc., Ph.D.; E. Garratt, M.Sc.; and T. E. Gardner, B.A., B.Sc.

Assistant—H. H. Froysell.

The Session commences October 5th.

Entrance Scholarship Examination takes place early in May each year.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in the University of Liverpool; for Degrees in Medicine of Liverpool; for the Pharmaceutical, Veterinary, Dental, and Public Health Diplomas; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry and other Examination Boards.

Lecture Courses.

A. General Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £4 10s.

Pharmacy Courses: Junior, £3; Senior, £3.

Course B.—Inorganic Chemistry. Fee, £3.

Course C.—Inorganic Chemistry (Honours Course). Fee, £2 10s.

Course D.—Organic Chemistry. Fee, £3.

Course E —Organic (Honours). Fee, £4.

Course F.—Physical Chemistry. Fee, £3.

Course G.—Honours Physical Chemistry. Fee, £4.

Course H.—History of Chemistry and Chemical Philosophy. Fee, £2.

Courses J. — Applied Chemistry and Metallurgy: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and other Inorganic Manufactures, including Fuel and Gas. (2) General Principles of Metallurgy. (3) Iron, Steel, and Aluminium. (4) Copper, Lead, Silver, Gold, and other Metals. (5) Technical Gas Analysis.

Course K.—Applied Organic Chemistry.

Course L — Applied Electro-chemistry.

Fee (Courses J, K, L), three terms, £2.

Practical Classes.

(1) Junior. (2) Intermediate: Qualitative Analysis; preparation of Inorganic Compounds; simple Quantitative and Volumetric Analysis. (3) Revision Class. (4) Engineers' Class. (5) General Metallurgy (Elementary).

Chemical Laboratory.

The Chemical Laboratories provide accommodation for every kind of chemical and metallurgical work and research. They include thirty rooms devoted to the study of Chemistry and Metallurgy. Separate rooms are provided for Organic Work, Quantitative Analysis, Water and Gas Analysis, Photometry and Photography, Metallurgy Laboratories, Research Laboratories and Library, and a Museum. Large new Laboratories for Physical Chemistry and Electro-chemistry have been recently erected.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided. Fees:—

Per Week.	One Term, Three Months.	Three Terms One Session.
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Whole week	10 10s.	21

D.P.H. Course (see special syllabus).

Course for Dental Degree (see special syllabus).

Technological Curriculum.

The curriculum extends over three or four years.

The Final Examination for the Associateship of the Institute of Chemistry may be taken after the third year. Those students who have taken the Ordinary Degree of B.Sc. may pass the M.Sc. Exam. in any subsequent year.

The Sheridan Muspratt Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1908, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the College Secretary not later than November 15. The Sir John Willox Chemical Scholarship, on similar lines, will be open for competition in December, 1909. Other Scholarships, Entrance Scholarships, and Free Student ships are also available to Students.

Evening Classes.

Classes on Metallurgy and Physical Chemistry will be held during the winter.

Prospectuses containing particulars may be obtainep from the Registrar, University of Liverpool.

ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE.

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S.

Lecturers in Chemistry—F. C. Garrett, D.Sc., F.C.S., and J. A. Smythe, D.Sc., Ph.D., F.C.S.

Assistant Lecturer and Demonstrator—A. A. Hall, M.Sc., Ph.D.

Lecturer in Agricultural Chemistry—S. Hoare Collins, M.Sc., F.I.C., F.C.S.

Assistant to Lecturer in Agricultural Chemistry—H. Crofts, B.Sc.

First Year Courses.—I. *General Course.*—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of

Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 7th. Fee, £3 10s. for the Session.

II. *Special Course.*—More advanced than the above. Wednesdays and Fridays, 11 to 12. Fee, £3 10s. for Session.

For Diploma in Electrical Engineering.—Tuesday, 12 to 1. A course of Lectures will be given dealing with the Principles of Chemistry, Fuel, the Phenomena of Combustion, and Metals and Alloys employed in Engineering, &c. Fee for the course, £2.

Second Year Courses.—The Lectures for the second year students consist of a course of Lectures on Organic Chemistry, and a course of Lectures on Inorganic Chemistry. The class on Organic Chemistry will meet on Tuesdays and Thursdays at 11 a.m., and will commence on October 6th. The class for Inorganic Chemistry meets at 11 a.m. on Mondays. Fee for Session, £3 10s.; for Inorganic alone £1 10s.; and for Organic alone £3.

Third Year Courses.—Advanced Classes are held for the study of Inorganic, Organic, and Theoretical Chemistry. Fee for the course, £3 10s.

A Lecture Course in Analytical Chemistry will be given on Fridays, at 9.15 a.m. Fee for the course, £1.

Metallurgy and Assaying.—Lecturer, Prof. Louis, M.A., D.Sc., F.I.C., F.G.S.; Demonstrator, H. Dean, A.R.C.M. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working two days, £3 10s. per term, £9 per session; one day per week, £2 per term, £5 per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the degree of Bachelor in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must have passed the University Matriculation Examination.

The University has recently adopted the following Matriculation Examination for students entering the Faculty of Science:—Additional Mathematics; English; English History; any *one* subject selected from Religious Knowledge, Botany, Zoology, Physical and General Geography, Experimental Science; any *two* subjects selected from Latin, Greek, French, German. (Students may substitute Extra Mathematics for one of these optional subjects up to and including September, 1911).

In order to enter on a three years' course of study for a Degree in Letters a student must have previously satisfied the Examiners in the following subjects:—Elementary Mathematics or Additional Mathematics; English; English History; either Latin or Greek; either French or German; *one* of the following subjects—Religious Knowledge, Botany, Zoology, Physical and General Geography, Experimental Science.

N.B.—(i.). Students who require to take three subjects to qualify for degrees in Science may offer any three of the following:—Additional Mathematics, Extra Mathematics, English, Latin, Greek, French, German, Physical, and General Geography, English History.

(ii.). Foreign Students may be exempted from the Matriculation Examination on report from the Council of the College of Medicine, or from the Board of Professors of Armstrong College, as the case may be, that they have already passed an examination equivalent to the Matriculation Examination of the University, and that they have sufficient knowledge of English to enable them to follow the courses of instruction they are entering for.

(iii.) Students from Oriental countries may be exempted from the Matriculation Examination on report from the Council of the College of Medicine, or from the Professors of Armstrong College, as the case may be, that they have received such an education in their own country as will enable them to profit by University study, and that they have sufficient knowledge of English to enable them to follow the courses of instruction they are entering for.

For detailed Syllabuses and complete Regulations the College Calendar should be consulted.

Bachelorship in Science.—Every candidate for the Bachelorship in Science will be required to satisfy the examiners in Mathematics, Physics, Chemistry, and either Geology or Natural History—in an examination to be held at the end of the candidate's first year, and at the end of the third year in an examination in one chief and two auxiliary subjects. For details of the subjects the College Calendar should be consulted. Candidates may qualify for the degree of B.Sc. by attending special courses in Agriculture, Engineering, and Mining, and passing the several examinations.

Exhibitions.—Two Exhibitions of the value of £20 and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Thursday, October 1st. Candidates should send in their names to the Secretary on or before September 12th.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

Several valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year, which is open to Bachelors of Science of any British University; the examination for this Scholarship will be held during the week commencing September 28th. Candidates should send in their names to the Secretary on or before September 20th.

THE UNIVERSITY OF MANCHESTER.

Professor of Chemistry and Director of the Inorganic Laboratories—Harold B. Dixon, M.A., M.Sc., F.R.S.

Professor of Chemistry and Director of the Organic Laboratories—W. H. Perkin, Ph.D., F.R.S.

Senior Lecturers and Demonstrators—G. H. Bailey, D.Sc., Ph.D.; J. F. Thorpe, Ph.D., F.R.S.; C. Weizmann, Ph.D.; Norman Smith, D.Sc.

Assistant Lecturers and Demonstrators—E. C. Edgar, D.Sc.; H. F. Coward, M.Sc; Ida Smedley, D Sc.; and J. L. Simonsen, M.Sc.

Professor of Metallurgy—H. C Carpenter, M.A., Ph.D.

Lecturer in Electro-Chemistry—R. S. Hutton, D.Sc.

The Session begins October 6, 1908.

The Chemical Classes form part of the Courses for Degrees in the University.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 9.30, during the Lent Term.

These courses are intended for Students commencing the study of chemistry.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30, during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, and Fridays, at 2, during the two Winter Terms. The Metals.

Third Year Honours Course.—Theoretical and Physical Chemistry.

Organic Chemistry (General).—Mondays and Fridays, at 9.30, during the two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Wednesdays, at 9.30, during the two Winter Terms.

History of Chemistry.—Short Courses during the two Winter Terms.

Metallurgy.—Introductory Course, followed by either—(A) Lead, Copper, Bismuth, Antimony, Zinc, and Tin; or (B) Iron and Steel. Each Course, one Lecture per week during the Session.

Electro-chemistry.—General Theoretical Course: Two hours per week during the Michaelmas Term.

Certificate in Applied Chemistry.—The course extends over three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

For further particulars of any of these courses apply to the Registrar, Edward Fiddes, M.A.

UNIVERSITY COLLEGE, NOTTINGHAM.

Departments of Chemistry and Metallurgy.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—R. M. Caven, D Sc., F.I.C.; G. Sand, D.Sc.; and G. Martin, Ph.D, B.Sc.

The Classes of the College are open to students of both sexes above sixteen years of age.

The Session commences in October, for both Day and Evening Classes.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Elementary Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

The fees for the Day Lectures and Classes are as follows: First year, two Lectures per week, 15s. per term. Second year, three Lectures per week, 22s. 6d. per term. Third year, four Lectures per week, 30s. per term.

Demonstrations and Lectures on Analytical Chemistry are given, and Chemical Calculation and Tutorial classes are also held. Various short courses of lectures on special subjects are delivered during the Session.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees for day students: For one term, £7; for the session, £18; for six hours weekly 40s., and 5s. extra for each additional hour per week. Evening students, 10s. for 2 hours per week, 3 hours 15s., 4 hours 20s., per term.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students are provided with Lectures and Laboratory work suitable for the preparation for the Minor and Major Examinations.

Evening Classes.—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tuesday and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, price one penny.

THE UNIVERSITY OF SHEFFIELD.

Professor of Chemistry—W. P. Wynne, D.Sc., F.R.S.

Lecturers and Demonstrators—W. E. S. Turner, M.Sc., B.Sc.; W. J. Jarrard, B.Sc.; C. R. Young, B.Sc.

The Session will commence October 7th.

Matriculation Course. — Tuesday and Friday at 9.30. Fee, £2 12s. 6d., and three hours per week Laboratory work.

Candidates for the Intermediate Examination are required to satisfy the Examiners in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, and Biology. And those for the Final Examination in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, Zoology, Botany, Physiology, Geology, Education.

Intermediate Course in Chemistry for B.Sc. or M.B.—Monday, Tuesday, Thursday, and Friday at 9.30 a.m. £5 5s., and nine hours per week Laboratory work.

B Sc. Course in Chemistry.—Monday at 9.30 a.m., Tuesday at 5 p.m., and Friday at 2.30 p.m., £4 4s., and 12 hours per week Laboratory work during two Sessions.

B.Sc. with Honours.—Honours Students in Chemistry, after passing the Intermediate Examination, devote the whole of their time to the study of Chemistry, and are expected to reach the standard for a pass in Chemistry for the ordinary degree by the end of the second year. During the second or third year they devote one day a week to lectures and practical work in a subsidiary subject—Mathematics, Physics, or Metallurgy—selected for the degree. The third year is devoted to the advanced study of Chemistry, either chiefly Physical and Inorganic or chiefly Organic, as the student may select. At least four days a week during the second and third years are spent in the laboratory.

M.Sc.—This degree may be conferred upon a Bachelor of Science with Honours who is of one year's standing from the date of his graduation as a Bachelor of Science, or upon any Bachelor of Science who has either passed an examination in an Honours School subsequent to graduation, or has for at least one year after graduation done research work at the University, and has presented a thesis, approved by the Faculty of Pure Science, upon the research work done during that period.

D.Sc.—The degree of Doctor of Science may be conferred upon any Master of Science of not less than five year's standing from the date of his admission to the degree of Bachelor, provided that he has published, in recognised journals or transactions, a research or researches of special merit and approved by the Faculty of Pure Science as qualifying him for the degree.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Three hours per week, £3 3s.; Six, £5 5s.; Nine, £7 7s.; Twelve, £9 9s.; Eighteen, £12 12s.; Twenty-four, £14 14s.; Thirty-two,

£16 16s.; Honour or University Students taking eighteen hours or more per week, £12 12s.

Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

A Course of Lectures, with a special class in Laboratory Work, is arranged for Medical Students entering for the Conjoint Board Examinations. Fee, £7 7s.

A course of Elementary Practical Physics and Practical Chemistry, which will meet the requirements of candidates for the Diploma of Public Health is held during the Michaelmas and Lent terms. Fee £5 5s.

An arrangement has been entered into with the Board of Education, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Board being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar of the University.

Evening Classes.—Lecture Class and Laboratory, on Wednesday evening during the Michaelmas and Lent terms. Fee, £1 10s.

Department of Metallurgy.

Professor—J. O. Arnold, D.Met.

Assistant Professor—A. McWilliam, M.Met.A.R.S.M.

This Department has been equipped to meet the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of Iron and Steel, Fuel, and Refractory materials. It also contains a complete pyrometric installation, and a laboratory for the study of the micrographic analysis of metals fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The School is now the most complete of its kind for teaching the practical manufacture, the chemical constitution, and the physical properties of Steel. Special attention is given to the determination of the microscopic constituents of Steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is not neglected, but is dealt with in a separate syllabus, dealing with metals (other than iron and steel) used in the arts. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates will be granted only to those who follow the prescribed courses, and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and on General Metallurgy. Practical Metallurgy:—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students in Collieries or Gas Works.

A new steel works has recently been erected in connection with the Sheffield College at a cost of about £15,000. The works include a two ton open-hearth furnace, a one ton Bessemer plant, and a four-hole crucible melting plant. The works is also provided with a hammer capable of dealing with four-inch ingots. Differential annealing furnaces and gas and electric hardening furnaces constitute part of the new plant. Additional laboratory accommodation is attached to the works, viz., chemical laboratory for staff, chemical laboratory for post graduate students, together with a complete magnetic laboratory for hysteresis, &c.

UNIVERSITY COLLEGE, DUNDEE.

University of St. Andrews.

Professor of Chemistry—(Vacant).

Assistant Lecturers—J. K. Wood, D.Sc., and T. Blackadder, B.Sc.

Lecture Assistant and Lab. Steward—J. Foggie, F.C.S.

The Winter Session begins early in October and ends in March. The Summer Session extends from the middle of April to the end of June.

The Junior Lecture Course on Systematic Chemistry is given daily during the Winter Session, and embraces the Elements of Inorganic and of Organic Chemistry.

Advanced Courses, of about fifty lectures each, will be given during the year as follows:—

Organic Chemistry; Inorganic Chemistry, including the more important technological applications; Theoretical and Physical Chemistry; Bleaching and Dyeing, including the Chemistry of the Textile Fibres.

Practical Instruction in all of the above branches will be given in the Laboratories and Dye-house. Special facilities are afforded to Research Students.

UNIVERSITY OF ABERDEEN.

Chemistry.

Professor—Francis R. Japp, M.A., LL.D., F.R.S.

Demonstrators—Francis W. Gray, M.A., B.Sc., and Joseph Knox, D.Sc.

I. *General Lecture Course* (100 *Lectures*).—Daily during the Winter Session. The subjects treated of include (1) The Laws of Chemical Combination and the General Principles of Chemistry; (2) Non-metallic and Metallic Elements, and their Compounds; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Fees, for first attendance, £4 4s.; for subsequent attendance, £3 3s. A Tutorial Class (without fee), conducted by the Junior Demonstrator, is held in connection with this course.

II. *Special Lecture Course on Organic Chemistry* (50 *Lectures*).—Daily during the Summer Session. Fee, £3 3s.

III. *Practical Course for Medical Students.*—This course, which occupies five hours a week during the Summer Session—in all fifty hours—is devoted to practice in Elementary Qualitative Analysis. Fee, £3 3s.

IV. *Chemical Laboratory.*—The Laboratory is open to Students daily from 9 a.m. to 5 p.m. Each Student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The Laboratory instruction includes: (1) General experiments; (2) Preparations; (3) Qualitative analysis; (4) Quantitative analysis: gravimetric, volumetric, and gasometric. The Course qualifies for the examinations of the Institute of Chemistry. Fee, £3 3s. a session. A certain number of free places are available, on the recommendation of the Professor, and subject to the approval of the Senatus, for research students.

V. *Physical Chemistry* (60 *Lectures*) —In connection with the Laboratory work, three Lectures a week on Physical Chemistry are delivered during the Winter Session by the Lecturer, Mr. F. W. Gray. Fee, £2 2s.

University of Aberdeen and Aberdeen and North of Scotland College of Agriculture.

Agricultural Chemistry.

Lecturer—James Hendrick, B.Sc., F.I.C.

Assistants—R. Glegg, B.Sc., F.I.C.; W. J. Profeit, M.A., B.Sc.; and John Macpherson, M.A., B.Sc.

I. Preparatory Courses in General Chemistry and in Organic Chemistry are given for those who are unable to take the full University Courses in these subjects. The course in General Chemistry consists of about sixty Lectures with Practical Work (one hour daily) during the Winter Session. The course deals with the general principles of Chemistry, and with those parts of Inorganic Chemistry which are of more immediate concern to students of Agricultural Chemistry. The Practical Work goes along with and illustrates the Lectures. Fee, £4 4s.

The course in Organic Chemistry consists of about thirty Lectures, and is given during the Winter Session. It deals especially with those parts of the subject which are directly related to Agricultural Chemistry. Fee, £1 1s.

II. *Agricultural Chemistry (General Course).*—This class meets daily during the Winter Session, and includes both Lectures and Laboratory Work. The Lectures deal with the Chemistry of the Atmosphere, the Soil, Manures, Foods, Preservatives, Insecticides, &c. The Physiological Chemistry of Plants and Animals, the Composition and

Manurial Requirements of Crops, and Dairy Chemistry are also treated of. The Laboratory Work is primarily intended to accompany and illustrate the Lectures. Exercises dealing with the properties and composition of Soils, Manures, Feeding-stuffs and Waters, and with the impurities and adulterations of these, occupy much of the time given to Practical Work. The fee for the whole Course (Lectures and Practical Work) is £4 4s.

III. *Laboratory.*—A Summer Course in Practical Chemistry is given to prepare students who have not previously done sufficient laboratory work for the course in Agricultural Chemistry. Fee, £2 2s.

IV. The Laboratory is open daily from 9 a.m. to 5 p.m. for students who wish to study the principles and practice of Agricultural Chemistry or to undertake research in this subject.

UNIVERSITY OF EDINBURGH.

Department of Chemistry.

Professor—James Walker D.Sc., Ph.D., F.R.S.

Lecturers—L. Dobbin, Ph.D.; H. Marshall, D.Sc., F.R.S.; and W. W. Taylor, M.A., D.Sc.

The working terms are—Winter Session, from beginning of October to middle of March; Summer Session, from beginning of May to middle of July.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical, arts, and science students is given by the Professor. The class meets daily; fee £4 4s. Advanced Courses of 25 lectures each are given in the Winter and Summer Sessions; fee £1 1s. An Intermediate Course of Organic and Advanced Inorganic Chemistry is held in summer; fee, £2 2s. There is also a class on History of Chemistry or Chemical Theory, by Dr. Dobbin; fee £1 1s.: and a class on Mineralogy and Crystallography, by Dr. Marshall; fee, £2 2s. All these Lectures, except the General Course, are now open to women, and a separate General Course for women in the faculties of Arts and Sciences has been arranged for the forthcoming Winter Session.

In addition to the above, Lecture Courses are from time to time given by the Assistants on particular branches of Organic and Inorganic Chemistry. These Lectures are free to Laboratory Students.

Laboratories.—Practical classes for Medical Students meet during the Winter Session and in the Summer Session. (Fee, £3 3s.) The laboratories for Science and Arts Students engaged in analytical and advanced practical work are open daily from 9.30 till 4.30. (Fees: Whole Day—Winter Session, £10 10s.; Oct.-Dec., Jan.-March, or Summer Session, £5 5s. Half Day—Winter Session, £6 6s.; Oct.-Dec., Jan.-March, or Summer Session, £3 3s. Preference will be given to students in the above order). Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry (including Gas Analysis), Physico-chemical Measurements, Agricultural Chemistry, and Assaying. Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical language, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination in Pure Science includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy (including Anthropology), Physiology, Geology (including Mineralogy), Zoology (including Comparative Anatomy), and Botany (including Vegetable Physiology). In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic, including Mineralogical, Chemistry; Organic Chemistry; Physical Chemistry; Chemical Crystallography; History of Chemistry. In the written papers a choice of questions is allowed, so as to adapt the examination to the various courses of advanced study which candidates may have selected. Practical Examination:—Complex Qualitative Analysis; Inorganic Preparations; Gravimetric and Volumetric Analysis. Each candidate taking the higher standard will also be examined on Organic Preparations, Ultimate Organic Analysis, and one of the following subjects, selected by himself:—Gas Analysis; Assaying; Physico-chemical Measurements, including Practical Crystallography as a special branch.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry *may be* required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. Laurie, M.A., D.Sc., F.R.S.E.

Professor—John Gibson, Ph.D., F.R.S.E.

Assisted by the following Lecturers and Demonstrators:—R. B. Denison, D.Sc., Ph.D.; Archibald Boon, B.A., B.Sc.; Andrew F. King, F.I.C.; E. B. R. Prideaux, M.A., D.Sc.

The Session begins October 1st, 1908.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Chemistry Course is designed to meet the wants of Manufacturing Chemists. The instruction consists of Courses in Chemistry, Physics, Mathematics, Engineering, and Mechanical Drawing, with Special Courses in Gas and Paper Manufacture, Brewing, &c., by Experts, in the fourth year. Special attention will be paid to Electrochemistry. The Chemistry Classes are recognised by the University as qualifying for the B.Sc., in Chemistry, and are also recognised by the Institute of Chemistry.

For Students who have been three and four years in the Chemistry Department, arrangements have been made for their spending from four to twelve months in the laboratories of the Corporation's Gas Works, with a view to the study of problems connected with the Combustion of Fuel, the Manufacture of Coal-gas and its By-products, &c.

A Laboratory, under the charge of Dr. Emil Westergaard, has been provided for the study of Technical Mycology, including Brewing, Distilling, Malting, Vinegar Making, Tanning, Preserving, Starch and Sugar Making, Bread Making, Butter and Cheese Manufacture, &c.

Matriculation Fee, 5s.; Composition Fees from £12 12s. to £15 15s. Full particulars are published in the Calendar of the College, which is issued early in September.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A.
Professor of Technical Chemistry—T. Gray, D.Sc., Ph.D.
Professor of Metallurgy—A. Humboldt Sexton, F.C.S., F.R.S.E.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

Session opens Sept. 21.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments. The diploma course in Chemistry extends over four years.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1908-1909 may be had from Mr. H. F. Stockdale, Secretary; price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

United College of St. Leonard and St. Salvator.

Professor of Chemistry — T. Purdie, B.Sc., Ph.D., LL.D., F.R.S.

The Session begins on October 7th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for about thirty-five Bursaries, ranging in value from £40 to £10 each per annum, will be held on September 11th and following days. Nineteen of these Bursaries are restricted to Men, two are open to Men or Women, and fourteen are restricted to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine.

A Hall of Residence is provided for Women Students.

Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree; the regulations will be found in the "University Calendar."

Lecture Courses.

Two distinct Courses of Lectures are given, each comprising at least one hundred meetings of the class.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment.

This course of instruction is intended to meet the requirements of the M.A., First Science, and M.B., Ch.B. Exams., so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part to General and Physical Chemistry, the instruction in general being such as is required for the Final Science Exam.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £4 4s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the Examinations in Arts, Science, and Medicine.

The fee for the Ordinary Course of Practical Chemistry is £3 3s. and for the Advanced Course £5 5s.

A special Research Department has been instituted by the University, the laboratories of which are open to students who give proof of their capacity of conducting chemical investigation.

QUEEN'S COLLEGE, BELFAST.

Professor — E. A. Letts, Ph.D., D.Sc., F.R.U.I., F.R.S.E., &c.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week, and terminate at the end of March The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry. Fee, £2.

II.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses. Fee, £3.

III.—*Laboratory Pupils.*—The Chemical Laboratory is open from November until the end of March, and from May 1st until the third week of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

The new Chemical Laboratories are now open, and are provided with all modern appliances. Special facilities are offered to those engaged in Research work.

Scholarships.—The following College Scholarships are awarded specially in connection with the schools of Chemistry and Physics:—Senior Scholarships in Chemistry alone awarded annually of £40, and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £80 annually, and tenable for two years. 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College every two years, of the annual value of £150. tenable for two or under special conditions for three years.

The following Scholarships, &c., of the Royal University of Ireland are awarded in the same group of subjects (Chemistry and Physics):—At the B.A. Degree examination, First-class Exhibitions of £42 each and Second-class Exhibitions of £21. At the M.A. Degree examination, a Studentship of £100 per annum, tenable for three consecutive years. Also a Junior Fellowship, tenable for four years, of the annual value of £200.

QUEEN'S COLLEGE, CORK.

Professor—Augustus Edward Dixon, M.D.
Demonstrator—John Taylor, M.Sc.

The College Session will commence in October, 1908, and end in June, 1909. All classes are open to male and female students.

The courses in Chemistry, though designed primarily to meet the requirements of candidates proceeding to the Examinations in Arts, Medicine, and Engineering of the Royal University of Ireland, of the Medical Licensing Bodies of Dublin and Edinburgh, and of the Pharmaceutical Society of Ireland, can be arranged specially as required, so as to render them suitable to any particular course of study. The following courses are provided:—

Systematic Chemistry.

I. General Lecture Course; three terms. Inorganic Chemistry, Elementary Organic Chemistry, and Chemical Philosophy.

II. Advanced Organic Chemistry, and Chemical Philosophy.

Practical Chemistry.

III. Winter Course of Practical Analytical Chemistry; commencing early in January, 1908.

IV. Summer Course of three months' duration, for students of Medicine; ending about the third week in June.

V. Course for Pharmaceutical Students; held during the second and third terms.

Laboratory Work.

VI. The Chemical Laboratory is open daily from 10 to 4 o'clock, except on Saturdays, to Students entering for Special Courses of practical work in General Inorganic Chemistry, Qualitative and Quantitative Analysis, Organic Chemistry, or for the purpose of Original Investigation.

Scholarships, &c.—In addition to the Class Prizes given at the Sessional Examinations, the College awards a Senior Scholarship of the value of £40, for Chemistry and Physics (either of which may be taken as a limited course), and numerous Junior Scholarships in Arts, Medicine, and Engineering, of which chemistry forms a part, value from £20 to £24 each, annually. The Royal University of Ireland also offers Exhibitions in Chemistry and Physics, First-class value £42, and Second-class value £21, together with other prizes, *e.g.*, a Studentship of £100 per annum, tenable for three years; and the 1851 Exhibition Scholarships, value £150, tenable for two, and, under certain circumstances, for three years, have from time to time been placed at the disposal of the College.

Full particulars as to Lectures, Fees, Scholarships, Exhibitions, &c,, are contained in the Regulations extracted from the College Calendar, which will be supplied on application to the Registrar.

QUEEN'S COLLEGE, GALWAY.

Professor—Alfred Senier, Ph.D., M.D., F.I.C., F.C.S., M.R.I.A.

Demonstrator—Rosalind Clarke, B.A.

Research Assistant—Frederick G. Shepheard, B.Sc., A.R.C.S., F.C S.

The Session commences in October and ends in June.

Chemistry is studied by attendance at Lectures, by work in the Laboratories, and by the use of the College Library. The Courses in the several faculties are arranged with a view to the requirements of the Royal University of Ireland, but are adapted also to those of other Universities and licensing bodies.

Lecture Courses. Faculty of Arts. — 1. Second year's Course, Inorganic and Organic, and the Elements of General Chemistry. 2. Third year's Course, Advanced Organic Chemistry. 3. Fourth year's Post-Graduate Course, Advanced General Inorganic and Organic Chemistry. *Faculty of Medicine.*—First year's Course, Inorganic and Elementary Organic Chemistry. *School of Engineering.*—First year's Course, Inorganic Chemistry.

Laboratory Courses. Faculty of Arts. — 1. Second year's Course, Exercises in Inorganic Qualitative Analysis. 2. Third year's Course, Quantitative Analysis and other experiments to suit the requirements of individual Students. 3. Fourth year's Post-Graduate Course, Advanced Quantitative Analysis, Organic and Inorganic Preparations, and determination of their Physical and Chemical characters. 4. The Laboratories are also open to Students for work in other branches of Chemistry. *Faculty of Medicine.* — 1. Second year's Course, Inorganic and Organic Elementary Qualitative Analysis, and the Chemical Examination of Urine. *School of Engineering.* —1. Second year's Course, Inorganic Qualitative Analysis.

A Scholarship in Chemistry is offered for competition each year of the value of £40, and Chemistry enters into the subjects required for numerous Scholarships in Arts, Medicine, and Engineering. The Royal Commissioners for the Exhibition of 1851 offer every two years a Science Research Scholarship of £150 per annum. This Scholarship has already been held by six Chemistry Students of this College.

For details as to Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar, published in December, and the Extracts from Calendar, published in advance in July, may be obtained.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

Dean of Faculty and Professor of Chemistry—W. N. Hartley, F.R.S., D.Sc.

Lecturer on Organic Chemistry—Alphonsus O'Farrelly, M.A.

Senior Assistant—J. Holms Pollok, D.Sc.

Junior Assistant—J. Ivon Graham, A.R.C.Sc.I.

The Royal College of Science supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Engineering (Mechanical and Electrical), Applied Chemistry, and Agriculture. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Applied Chemistry is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Chemistry; (2) Organic Chemistry, Elementary and Advanced; (3) Analytical and Experimental Chemistry; (4) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£5 for three months; £9 for six months; £12 for the entire session. For Assaying—£5 for three months; £9 for six months. £12 for the entire session.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College.

A limited number of Scholarships in Science and Technology are competed for each year. These Scholarships include free education for the full Associateseip Course of three years and maintenance allowance of a guinea a week during the Session.

PROFESSIONAL CHEMICAL QUALIFICATION (F.I.C. AND A.I.C.).

The Institute of Chemistry of Great Britain and Ireland.—The Institute of Chemistry was founded in October, 1877, and incorporated by Royal Charter in June, 1885, (i.) to promote the better education of persons desirous of becoming professional consulting and technological chemists, public analysts, and chemical advisers; (ii.) to examine Candidates, and to grant certificates of competency; and (iii.) to elevate the profession of Consulting and Analytical Chemistry by setting up a high standard of scientific and practical proficiency and by insisting on the observance of strict rules in regard to professional conduct. *The Studentship.*—Every Candidate for admission to the Studentship is required to produce evidence that he is at least seventeen years of age, and that

he has passed a Preliminary Examination in subjects of general education, recognised by the Council of the Institute. He must also show that, at the time of making application for registration, he is working at a College or University recognised by the Council, or under the direction of a Fellow of the Institute in an approved laboratory, with the object of adopting the profession of Analytical and Consulting Chemistry. *The Intermediate Examination in General Theoretical and Practical Chemistry.*—Candidates for admission to the Intermediate Examination are required to produce evidence (I) of having passed an approved Preliminary Examination in subjects of general education; (II.) of having regularly attended systematic day courses, in a College or University recognised by the Council, during at least three academic years, in theoretical and practical Chemistry, and courses in Physics, Mathematics, and one of the following subjects, in accordance with the Regulations of the Institute: (i.) Higher Physics; (ii.) Advanced Mathematics; (iii.) Mechanics and Chemical Engineering; (iv.) Metallurgy; (v) Geology and Mineralogy; (vi.) Physiology; (vii.) Bacteriology; (viii.) Agriculture; (ix.) Elementary Botany; (x.) Elementary Biology; and (III) of having satisfactorily passed the Class Examinations in all the subjects required to be taken. As an alternative in the matter of training (II.), a candidate may take two years' training in a recognised Institution as indicated above, and work systematically for two other years under a Fellow of the Institute in an approved laboratory. A Candidate who has taken a Degree in Science (including Inorganic and Organic Chemistry, and Physics in the Degree Examination. Mathematics having been also passed in at either the Final or Intermediate University Examination) in a University recognised by the Council, is eligible for admission to the Intermediate Examination of the Institute. Holders of certain Honours Degrees or Diplomas are exempt from passing the Intermediate, and, by virtue of their qualifications, are eligible for admission to the Final Examination direct. *The Final Examination for the Associateship (A.I.C.).*—This comprises, in addition to a general knowledge of all branches of chemistry, a thorough knowledge of one branch—mineral chemistry; metallurgical chemistry, physical chemistry, organic chemistry, analysis of food and drugs and water (including a compulsory examination in therapeutics, pharmacology, and microscopy), or biological chemistry. Any Candidate who has passed the Intermediate Examination of the Institute, or who is entitled to claim exemption from passing the Intermediate Examination, is eligible for admission to the Final Examination. *Fellowship (F.I.C).*—For admission to the Fellowship, an Associate is required to have been registered for three years, and to have been continuously engaged during that period in the study and practical work of Applied Chemistry in a manner satisfactory to the Council. Full particulars are given in "The Book of Regulations for the Admission of Students, Associates, and Fellows," which may be obtained (Price One Shilling) from the Registrar, 30, Bloomsbury Square, London, W.C.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE FOR THE ADVANCEMENT OF TECHNICAL EDUCATION.—The operations of the City and Guilds of London Institute are divided broadly into four branches: the educational work of three London Colleges, and of the Technological Examinations. Programmes of the London Colleges may be had on application to the Head Office of the Institute, Gresham College, Basinghall Street, London, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. The Programme of the College, containing full particulars of the conditions of entrance, fees, and courses of instruction, may be had on application. *City and Guilds Central Technical College, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph.D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examinations begin on Tuesday, September 22nd, and the Winter Session opens on Tuesday, September 29th, *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. An examination for the admission of Students will be held at the College on Tuesday, September 22nd. Session begins September 29th. *South London Technical Art School.* — Classes in Modelling, Design, Drawing and Painting, House Decoration.

CITY OF LONDON COLLEGE, White Street, Moorfields.—I. S. Scarf, F.I.C., F.C.S., and Assistants. Courses of Saturday and Evening Lectures and Laboratory Practice in Chemistry and Physics, open to Students of both sexes. Day Commercial School commenced Sept. 14. Session commences September 28th.

BATTERSEA POLYTECHNIC.—Principal, Mr. S. G. Rawson, F.I.C. Inorganic, Organic, and Technological Chemistry, Mr. John Wilson, M.Sc. (Vict.), and Assistants. Session opens Sept. 21. Complete courses of Instruction are given in Chemistry (Inorganic and Organic), together with Physics, Electricity, Engineering subjects, German, &c., for intending technological and works chemists. Certain of the Courses (Day and Evening) are recognised by the University of London in preparation for the B.Sc., for which examination (Pass and Honours) complete courses of instruction, under recognised teachers, are provided. Special Evening Courses in Technical Bacteriology, Paper Making, and Oils, Fats, Soap, and Candle Manufacture.

BOROUGH POLYTECHNIC INSTITUTE, 103, Borough Road, S.E. — Chemistry: Evening Lectures and Laboratory Work in Inorganic and Organic Chemistry (Session fees, per course, 10s. to 15s.); Electrochemistry; Dr. F. Mollwo Perkin, assisted by H. D. Law, B.Sc., and C. T. Bennett, B.Sc. Electricity and Magnetism, and Electro-technics: Evening Lectures and Laboratory Work (Session fees, per course, 10s. to 15s.), Dr. J. Henderson, assisted by H. Saunders. Special Evening Courses on Painters' Oils, Colours, and Varnishes. Session opens Monday, Sept. 28.

Birkbeck College, Breams Buildings, Chancery Lane.—Chemistry Courses conducted by Dr. Alex. McKenzie prepare for various Examinations, the B.Sc. and M.B. Degrees of the London University, Conjoint Board, Pharmaceutical Examinations, Board of Education, &c. The Session will commence on Monday, Sept. 28, when Dr. Albert Griffiths will give the Opening Address, at 7.30 p.m. The Day and Evening courses of study include Chemistry, Physics, Botany, Zoology, Geology, Mathematics, Latin, Greek, Modern Languages, Economics, Geography, Logic, and various branches of Law. Courses conducted by recognised teachers of the University provide for the Examinations of the University of London, in the faculties of Arts, Science, Commerce, and Law. Courses in Mining, Metallurgy, and Assaying are given both in the day and evening. The Modern Language classes include Italian, Spanish, and Portuguese, as well as French and German. The College possesses a School of Art, open both day and evening. The Calendar supplies detailed information respecting the Courses of Study, Examinations, Studentships, &c.

Northern Polytechnic Institute, Holloway Road, N.—Principal, R. S. Clay, D.Sc.; Head of the Chemical Department, W. H. Mills, M.A., Sc.D.; Assistants, W. H. Watson, B Sc., A.R.C.S.; Miss A. M. Bain, M.A., B Sc.; F. W. Linch, A.I.C. The Chemical Department contains three fully equipped laboratories for Elementary, Intermediate, and Advanced and Research Work respectively. Systematic Day and Evening Courses are conducted for the London University Degrees, Pass and Honours, as well as for the Board of Education Examinations. The new Session begins September 16 Full information respecting the classes is to be found in the Prospectus, which will be sent free on application to the Secretary.

Northampton Polytechnic Institute, St. John Street Road, E C.—Principal, R. Mullineux Walmsley, D.Sc, &c.; Technical Chemistry, Mr. S. Field, A.R.C.S.; Mr. A. H. Munday, F.C.S.; and Mr. G. Naylor. Day and Evening Classes in Electro-chemistry, Electro-plating, Electro-metallurgy, Electrotyping, and Stereotyping. (For full details see Prospectus).

South Western Polytechnic, Chelsea, S.W.—Principal, Sidney Skinner, M.A. Head of the Chemical Department, J. B. Coleman, A.R.C.S., F.I.C. Day and Evening Courses in Theoretical and Practical Chemistry and several branches of Applied Chemistry including Metallurgy, Assaying, Photography, &c. Systematic Courses are held for the Matriculation, Inter. Sci., and B.Sc. Examinations (Pass and Honours) of the University of London. The Day Course in Chemistry is of three years' duration; it gives a thorough training to those who wish to become Consulting or Industrial Chemists. Prospectus of Day and Evening Classes may be obtained from the Secretary, 1d., by post 4d.

East London College, Mile End Road, E.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D. Lectures and Practical Classes are conducted in the Day Technical College, the regular College Course being three years. The work of the first year corresponds with the requirements of the Int. Sci., Lond., that of the next two years with the degree examination, B Sc. (Honours and Pass). Special attention is given to work for the Honours Examination and research. Evening Classes for London University Degrees are also held.

University Tutorial College, 32, Red Lion Square, Holborn, W.C.—This Institution contains large Laboratories for Chemistry, Physics, Geology, and other subjects. Classes are specialised for Examinations of London University, but students may take up work for any Examination. The special feature of the College is that work goes on all the year round, thus affording students residing in the Country an opportunity of doing practical work during their Vacations.

The Polytechnic, 309, Regent Street, W.—University of London Preparation Classes.

Sir John Cass Technical Institute, Jewry Street, Aldgate.—Principal, Charles A. Keane, D.Sc., Ph.D., &c., assisted by H. Burrows, Ph.D., F.I.C., Arthur R. Ling, F.I.C., R. S. Willows, D.Sc., C. O. Bannister, A.R.S.M., Arthur Harden, D.Sc., A. E Hall, A.R.C.S., and Wesley J. Lambert. The Institute is conveniently situated for those who work or live in the Eastern Districts of London; it was founded by the Governors of Sir John Cass's Foundation, and forms one of the Polytechnics aided by the London County Council. The instruction is especially devoted to technical training in experimental Science and in the Artistic Crafts, graded curricula of study, extending over several years, being provided in Pure and Applied Chemistry and Metallurgy, and in the various forms of craft work, including Art Metal work, Jewellery, Enamelling, Bronze casting, Chasing; full courses of study are also provided in Drawing, Design, and Modelling in connection with these crafts, Drawing and Modelling from living animals being a special feature of this work. There is also a full course of instruction for the B.Sc. Degree of London under recognised teachers of the University. Commercial Classes, including Modern Languages, are provided to meet the requirements of those engaged in City Offices. Classes begin September 21. Full details may be obtained on application, or by letter to the Principal.

Imperial College of Chemistry and Pharmacy, 49 and 51, Imperial Buildings, Ludgate Circus.—Mr. F. Davis, B.Sc. An especial course of instruction is given at this College in Pharmacology and Therapeutics, *re* the Institute of Chemistry Examination. Students attending the College visit technical works.

Blackburn Municipal Technical School.—Chemistry: Mr. Robert H. Pickard, D Sc.(Lond.), &c., assisted by Messrs. Jos. Yates, M.Sc., W. O. Littlebury, F.I.C., Jos Kenyon, B.Sc., A.I.C., and W. A. Jowitt. Session opens Monday, Sept. 21. Full details of the Classes are given in the "Students' Handbook," which may be had at the Institution (price 1d., by post 3d).

Leeds: Central Technical School, Leeds Institute, Cookridge Street, Leeds.—Head Master, R. E. Barnett, B.Sc. (Lond.), A.R.C.S. Evening Classes are held in all subjects of Science and Technology, among which are:—Chemistry (Inorganic and Organic), Chemical Calculations and Principles of Analysis, by Mr. R E. Barnett, B.Sc., A.R.C.S., Mr. J. B. Murray, Mr. A. McFarlane, and Mr. O. F. Kirby, M.A., B.Sc.; Metallurgy (Theoretical and Practical) and Iron and Steel Manufacture, by Mr. B. A. Burrell, F.I.C., F.C.S.; Gas Manufacture, by Mr. W. E. Pettigrew; Oils and Fats, by Mr. W. Dillon; Magnetism and Electricity, Practical Physics, &c., by Mr. J. E. Tindall, B.A., B.Sc.; Bread-making and Flour Confectionery, by Messrs. W. H. Quinn and J. C Hasselgrave; Photography, by Mr. S. E. Bottomley. Fees: from 7s. 6d. per session. Group courses arranged for Students engaged in Chemical Industries. Special three evening Course for Pharmaceutical Students, covering the "Minor" syllabus in three years, by Messrs. J. H. Gough, Ph.C., F.C.S.; S. Parrish, B.Sc., A.R.C.S; and N. Walker. Session commenced Sept. 14th. See the Technical Handbook, 2d. (by post 4½d.). Prospectuses of various Classes free on application to the Head Master, or to Mr. James Graham, Secretary for Education, Calverley Street, Leeds.

City of Leeds Higher Education Department.—Courses of Evening Classes have been arranged for the Minor Examination of the Pharmaceutical Society, in which the whole Syllabus will be covered in three Winter Sessions. Chemistry: Mr. S. Parrish, B.Sc., A.R.C.S., Chief Lecturer in Chemistry, Central High School, and Mr. J. B. Murray. Botany: Mr. Norman Walker, Assistant Lecturer in Botany, Leeds University. Pharmaceutics: Mr. J. H. Gough, Ph.C., F C.S., Demonstrator in Materia Medica and Pharmacy, Leeds University. Full particulars from Mr. James Graham, Secretary for Education, Education Offices, Leeds.

Redruth School of Mines, Cornwall.—Principal, Howard C. Ridding, A.R.S.M., F.I.C., assisted by a staff of Mining Engineers and Mine Surveyors Courses of Practical and Theoretical instruction are given in Inorganic Chemistry, Assaying, Mineralogy, Blowpipe Analysis, Mine Surveying, Geology, Principles of Mining, Ore Dressing, Mechanical Engineering, &c., for intending Assayers, Mineral Chemists, Mining Engineers, and Surveyors. Shorter Courses are also held in the above-named and cognate subjects to meet the requirements of those having a limited time at their disposal and Prospectors. Practical instruction in Mining given at the Basset Mines, Ltd. Syllabus on application to the Registrar. Session commences Wednesday, Sept. 16.

Municipal School of Technology, Sackville Street, Manchester.—Laboratories and workshops for Mechanical, Electrical, Sanitary and Hydraulic Engineering, Textile industries, Photography, Collotype and Photo mechanical processes, Letterpress and Lithographic industries, and industries within the scope of Architecture. The provision for the teaching of Chemistry, as might be expected in a district where the Chemical industries are important, is of an exceptionally complete character. It comprises laboratories for Metallurgy, Brewing, Bleaching, Dyeing and Printing, Paper-making, and Electro-chemistry. The Bleaching, Dyeing, Printing and Finishing, and the Paper-making industries are in addition extensively equipped in a separate building with machinery and appliances on an industrial scale. A Brew-house is also equipped on the low gravity principle, with a plant of four bushel capacity. The School is now established as the Faculty of Technology in the University of Manchester, and students of the School fulfilling the conditions can proceed to the Degrees of Bachelor and Master of Technical Science B.Sc. and M.Sc. Tech.). The Session commenced Sept. 14

Wolverhampton Municipal Science and Technical School.—Inorganic and Organic Chemistry, Mr. W. Whitehouse, F.C.S.; Physics, Messrs. W. Whitehouse and A. T. Harrison, B.Sc.; Botany, Mr. Sidney Phillips, Ph.C. Day Classes in Chemistry, and Evening Classes in Chemistry, Physics, Botany, French, &c. Special arrangements are made for the requirements of Pharmaceutical and Medical Students. Session commenced Monday, Sept. 14th. For other particulars and programme, apply Mr. G. F. Chell, Secretary.

Iron and Steel Institute.—In addition to the papers already announced for reading at the Middlesbrough Meeting of the Iron and Steel Institute on September 29 to October 1, a paper will be presented by Mr. William Hawdon (Middlesbrough) on "The Progress in the Cleveland Iron and Steel Industries during the past Quarter of a Century," that is, since the previous visit of the Institute to Middlesbrough in 1883. The paper promised by Mr. J. E. Stead and Mr. T. Westgarth will be held over until the next meeting.

The Chemical Laboratory Fresenius at Wiesbaden.—During the Summer Term, 1908, the Chemical Laboratory Fresenius was attended by twenty-five students. Of these eleven were from Germany, four from Russia, three from the United States of America, two from England, one from Austria, one from Switzerland, one from Sweden, one from Norway, and one from East India. There were two assistants in the Instruction Laboratory, and twenty-two in the Versuchsstationen (Private Laboratories). To the certified staff of teachers belong the Directors, Geh. Regierungsrat Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Hintz, and also Prof. Dr. med. G. Frank, Dr. L. Grünhut, Dr. R. Fresenius, and J. Huber (Architect). The next Winter Term begins on October 15th. Ladies are also admitted as students. During the past Summer Term, besides the scientific researches, numerous analyses were undertaken in the different departments of the Laboratory (Versuchsstationen) on behalf of trade, manufacture, industry, mining, agriculture, hygiene, justice, and government.

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SESSION 1908-1909.

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LITHIUM IN RADIO-ACTIVE MINERALS.*

By Prof. W. N. HARTLEY, F.R.S., Royal College of Science, Dublin.

The question whether lithium is, or is not, a widely occurring element in nature, and whether it is found associated with any other element, more particularly with copper than with the alkalis or the alkaline earths, arises from the assumed transmutation of copper contained in solutions which were exposed to the radiations of radium into lithium, neon, and possibly other substances.

In the course of a discussion on the subject it has been stated by Sir William Ramsay (*Nature*, March 5th, 1908, p. 412) :—As sodium and potassium are much more widely distributed than lithium, it is more likely that they are the chief products from copper, and that some modifying circumstance has determined the formation of a trace of lithium. Lithium was mentioned because it is an unlikely constituent of dust, glass, copper, &c., which were tested specially to prove its absence."

There are two distinct statements here which, according to wide experience, appear to require modification. .

First, is it the fact that sodium and potassium are much more widely distributed than lithium ?

They appear to be more abundantly distributed, but that is not the question. Let us take, first, the evidence of Kirchhoff and Bunsen on this point (*Pogg. Ann.*, 1860, cx., 161).

It was experimentally proved that the eye can detect 9/1,000,000 of a mgrm. of lithium carbonate suspended in the air of a room in which a Bunsen flame was burning, the quantity of sodium chloride perceived in similar circumstances was 1/3,000,000 of a mgrm. ; in other words, the sodium chloride flame reaction is twenty-seven times as delicate as that of lithium carbonate.

If these figures be taken for calculating the quantity of lithium and sodium respectively which colour the flame, it will be found that the proportions are approximately 1/600,000 of a mgrm. and 1/1,200,000 ; so that the reaction for sodium is at least twice as sensitive as that for lithium. The eye is, however, much less sensitive to the red line of lithium than to the yellow line of sodium when the two substances are mixed.

Kirchoff and Bunsen state that lithium is one of the most widely distributed elements in nature, and proceed to substantiate this view. Thus, the presence of lithium was easily detected in 40 cc. of sea-water taken in long. 39° 14′ W. and lat. 41° 41′ N. ; in the ashes of seaweed carried by the Gulf Stream to the coast of Scotland ; in all varieties of orthoclase and quartz from the granites of the Odenwald ; in spring-water from the eastern slopes of the Neckar, near Heidelberg. The laboratory water supply did not contain it, because it came from a different geological source. It was found in the ashes of all kinds of wood, the trees of which grow on a granitic soil ; it was found also in varieties of potash from Russia and elsewhere ; in the ashes of tobacco, and the leaves and tendrils of the vine ; in the ashes of cereals of all kinds grown on granitic soil on the plain of the Rhine ; in the blood and muscle of ruminant animals, and likewise of man. Subsequently, it was detected in a few decigrms. of the solid residue of sea-water,† and in many mineral waters, in different varieties of marble, and in many calcareous rocks, also in English chalk. Traces of lithium were also found in potash-glass.

More recently, evidence has been derived from facts which may be divided into three categories. First, those observed in the spectroscopic and spectrographic analysis of common ores and minerals from different parts of the world, and such as are not associated with the alkali metals or with radio-active substances. Mr. Ramage and I examined more than 170 of these substances, and without exception they all contained sodium and potassium, and the potassium almost invariably contained lithium ; but a more remarkable fact was brought to light by the detection of rubidium along with potassium, lithium, and sodium. The lines of potassium and rubidium were photographed, but the photographic plates were not sufficiently sensitive to the lithium red line ; it was therefore, as a rule, observed by the eye only ; that is to say, spectroscopically, but not spectrographically. But whenever the rubidium line or lines were photographed, the red lithium line was invariably visible with the spectroscope. Thus, in sixty-two iron ores, rubidium was found in sixty-one. In sixteen red hæmatites, which are among the purest minerals found in the massive state, rubidium was detected in three. In seven magnetites, rubidium was contained in four. In seventeen aluminous minerals containing only very minute traces of potassium and sodium, rubidium was not detected. All the 170 minerals described contained copper, and of these 153 contained silver likewise. Lithium therefore was associated with copper, and likewise with silver. The presence of lithium was invariably observed in the spectra of the Bessemer flame, the number of observations certainly exceeding 100. Facts of the second kind relate more particularly to the salts of the alkalis ; the crude material from whatever source invariably contains lithium ; and many potassium salts, whether re-crystallised or otherwise, contain lithium and rubidium, and, not rarely, cæsium also.

Facts of the third category are derived from experimental evidence which is quantitative and spectrographic. With Wratten and Wainwright's plates (pinachrome bathed), which I have used for the last three years, it is possible to photograph far into the red, so that not only the potassium line λ 7667, but also the brownish red pair of rubidium lines with wave-lengths 7950·46 (Lehmann) and 7799 (Ramage) may be photographed with ease.

For some years past I have been engaged in determining the spectra obtained by operating on definite quantities of different salts, and am in a position to state the minimum weight of certain of the elements contained in each ore or mineral analysed, a weighed quantity of 0·5 grm. having been taken for each analysis.

The following passages refer to numbers taken from a communication read on June 16th, and since published by the Royal Dublin Society :—

Lithium.—When there are four lines visible on the photograph, namely, λλ 7608, 4603·07, 4132·93, and 3232·82, there cannot be less than 0·0089 grm. of lithium present in the flame. When the lines λλ 6708·0 and 4603·07 are visible, the quantity is not less or more than 0·041 grm. of lithium. When only the red line appears, the quantity is not more than 0·002 grm., and with half this quantity the red line ceases to be photographed.

Hence the quantity present, even when the red line is not photographed, may be as much as 0·001 grm. in 0·5 grm. of substance, or 2 parts of lithium in 1000 ; that is to say, 0·2 per cent. When care is taken to separate the alkalis this proportion is rendered much smaller.

The photographs were very generally taken upon Edwards's isochromatic plates, or those of Cadett and Neale ; consequently the quantitative results with lithium and potassium are not comparable with those obtained more recently with Wratten and Wainwright's panchromatic plates. For instance, the most persistent line on the lithium plates was λ 4603 in the blue ; now it is the red line λ 6708 which still appears strong after the blue line has ceased to be photographed ; the spectrographic reaction therefore is now much more delicate.

* A Paper read before the British Association (Section B), Dublin Meeting, 1908.

† It may be stated here that a marine boiler incrustation deposited from sea-water was found by spectroscopic analysis to contain calcium and strontium, the latter in the proportion of about 1 per cent. But neither Mr. Ramage nor I, who both examined this material independently, could detect the presence of any lithium, the explanation being that it had remained dissolved in the water in the form of sulphate.

Potassium.—The ultimate line, that is to say the most persistent one in this spectrum, is λ 4047·39, and this is not photographed with less than 0·0000004 grm. of the element; this, when operating on 0·5 grm., indicates the presence of 0·00008 per cent of potassium. The flame reaction for potassium is therefore seen to be about forty thousand times more sensitive than that for lithium.

Rubidium.—Similar results were obtained with rubidium salts. All potassium salts not specially prepared as already stated were found to contain this element. The two rubidium lines 4215·8 and 4202·4 almost coincide with two iron lines, 4216·3 and 4202·1. When much iron is present it should be separated, but in instances where the penultimate line is visible, but the ultimate line is obscured by an iron line, this is not necessary because we know that this latter line must be there by reason of its being the stronger of the two rubidium lines. When these two lines are visible but very faint, there cannot be more than 0·00001 grm. of rubidium present. Smaller quantities are detected by the visibility of the ultimate line with wavelength 4202·4.

The connection between rubidium and lithium is this: that in whatever substance the less refrangible of the rubidium lines was photographed, lithium was detected by eye observations made on the flame with the spectroscope.

The question whether lithium is likely to occur or does occur in dust, may be answered by giving a list of substances in which it has actually been found.

It was found in mother-liquors from which potash-alum had been crystallised. In Donegal kyanite, which contains 98 per cent of aluminium silicate; in the quartz, felspar, and mica of granite from the Dublin and Wicklow mountains; in asbestos; in barytes from Duneen Bay, Clonakilty; in kaolin from Devonshire; in ordinary clay tobacco-pipes; in clay from decomposed quartzite found at Shankhill, Co. Dublin; in bauxite from France, and from Co. Antrim; in beryls from Glencullen, Co. Wicklow; and in many and various limestones.

In the Bessemer Flame.—At Crewe works of the London and North-Western Railway Company; at Middlesbrough in the Cleveland district of Yorkshire, and in South Wales.

In Atmospheric Dust.—In dust which was precipitated in sleet, hail, snow, and rain respectively, which fell in Dublin. It was not found in a specimen of meteoric dust which fell from the clouds, but it has been detected in some specimens of stoney meteorites, and in volcanic dust.

In Flue Dust.—In was found in flue dust from Crewe gasworks; Boyd's Chemical Works, Dublin; Nicholson's Copper Smelting Works, Leeds; ferro-manganese furnaces, Pittsburg, U.S.A.; ferro-manganese furnaces in England; Cleveland blast-furnaces; basic iron furnaces; and in South Wales iron furnaces; in the ashes of plants; in coal-ashes; also in soot from domestic chimneys. In short, twenty-four specimens of dust all contained lithium, and in nineteen of these rubidium was also detected. It was found in roasted shale and in smaltine. It occurs likewise in the gault of Cambridgeshire, as was ascertained by the late Sir George Stokes. Metallic calcium always contains it, and I have found it in a specimen of metallic palladium prepared by Wollaston the discoverer of this metal. It may be mentioned here that a careful examination of photographs taken of the oxyhydrogen flame spectra of flue dust from copper works enabled Mr. Ramage and myself to identify the following elements and determine their presence:—Sodium, potassium, lithium, rubidium, cæsium, copper, silver, calcium, strontium, aluminium, gallium, indium, thallium, iron, nickel, cobalt, manganese, chromium, lead. zinc, cadmium, and tin. Metals of the alkalis are not unfrequent constituents of heavy metals obtained by smelting processes; potassium occurs, for instance, in iron and steel; in the latter metal it was proved to be more than a mere surface contamination by immersing a new file in hydrochloric acid so as to remove any traces of adhering dust, washing thoroughly in pure distilled water, and burning the file in the oxyhydrogen flame.

One or two practical points occur to me to be worth mentioning. The spectrograph has a train of four quartz prisms of 60°, each one being composed of two halves cut from crystals of right and left-handed rotation; the collimator and camera lenses are also of opposite rotation, and have a focal length of about 12 inches for the D line; the dispersion and fine definition are such that with minute quantities of sodium the two yellow lines appear on the photographs so well separated that the distance from one to the other measures 0·42 mm. with a difference in wavelength of 6 Angström units.

Secondly, the supports used are pure ashless filter-papers 15 cm. in diameter, ten of which show nothing of a metallic nature when burnt but the sodium lines and possibly a trace of calcium.

It is not usual to take more than one of these filter-papers, and that is burnt in two halves; they are protected from any possible contamination through dust settling on them. All reagents used were prepared for the purpose, and blank experiments were made with them; moreover, all chemical reactions were carried out in platinum vessels.

I am therefore unable to corroborate the statement that sodium and potassium are elements much more widely distributed than lithium, or that lithium is an unlikely constituent of dust, glass, or solutions of copper, because all evidence obtained from flame spectra at high temperatures leads entirely to a contrary conclusion.

Moreover, there does not appear to be any obvious or particular connection between lithium and the radio-active elements, seeing that the former is "one of the most widely distributed elements in nature," and that, beside the alkali metals, we must place the following metallic elements:—Calcium, copper, silver, lead, manganese, aluminium, gallium, and iron.

COLLOIDAL CHEMISTRY.*

By H. R. PROCTER, M.Sc.

MODERN colloidal chemistry may be said to begin with the work of Graham about 1861, though the colloids had long been known to chemists, and Faraday (*Phil. Trans.*, 1857, i., 145) had prepared and described colloidal gold solutions. Graham first pointed out the radical differences between the colloid and crystalloid state, and introduced most of the nomenclature now in use, such as "sol" and "gel" for the apparent solution and the precipitate or jelly, and distinguished their various liquid media by the prefixes "hydro-," "alco-," &c. It would be impossible to refer in detail to the various workers who have since contributed to its advance, but the following may be mentioned as marking distinct steps in its progress. Wiedemann (*Verh. d. Physik. Ges. zu Berlin*, 1884, p. 44) showed that the absorption of water by solid colloids is in its earlier stages accompanied by considerable evolution of heat, actual solution and the fusion of jellies by absorption, while in gelatinisation heat is evolved. He later published researches on electrical osmose and cataphoresis which have important bearings on colloidal theory. The work of Van Bemmelen, 1888 *et seq.*, on colloidal jellies and precipitates is of permanent value, and his theory of the network or cellular structure of jellies has been very generally accepted by later workers, though, in your reporter's opinion, on insufficient evidence. In 1889 M. Carey Lea published extensive researches on "allotropic" (colloidal) silver (*Silliman's Journ.*), and in 1892 Picton and Sinder's work on "Solution and Pseudo-solution" (CHEMICAL NEWS and *Journ. Chem. Soc.*) opened new ideas on the nature of colloidal solution, and perhaps of solution in general. In 1893 Siedentopf and Zsigmondy,

* A Paper read before the British Association (Section B), Dublin Meeting, 1908.

building on the earlier work of Tyndall on the scattering and polarisation of light by non-homogeneous media, invented the ultramicroscope, in which, by a special form of dark-ground illumination, particles which were much too small to give an actual microscopic image were rendered visible as points of light. By this means the suspended matter in many colloid solutions has been rendered visible and the number and size of the colloid particles estimated.

Since sodium and potassium chlorides have been obtained in colloidal form in organic solvents, it is no longer possible to distinguish between colloid and crystalloid *substances*, but only between the colloid and crystalloid *state*. In the typical crystalloid solution of an electrolyte the dissolved body is separated into its molecules, and to a large extent into individual ions, while in the colloid sol the units of distribution are either large and often conjugated molecules or more frequently minute particles composed of many molecules united by cohesive attraction. Whether there is in principle any clear line dividing these conditions, or whether they do not rather shade off into each other by insensible gradations, is very doubtful, but in typical cases the distinction is sufficiently marked. As osmotic pressure and all its attendant effects are proportional to the *number* of the dissolved molecules, and therefore for a given quantity of substance inversely to the mass of the molecules or particles, these physical effects are almost absent in the colloid sol, and in most cases diffusion, lowering of freezing-point, raising of boiling-point, and *a fortiori* electric conductivity which demands ionic dissociation, are barely, if at all, perceptible, and may perhaps be attributable to the traces of electrolyte which appear essential at least to inorganic colloid solution. In the cases of many organic colloids of known high molecular weight, boiling- and freezing-point determinations have yielded numbers not inconsistent with the view that the particles are actual single molecules. While crystalloid bodies can usually only be separated from solution by evaporation or freezing of the solvent, or by chemical changes, colloid sols are unstable, and liable, either spontaneously or through very slight disturbing causes—such as the addition of an electrolyte, change of temperature, or concentration—to separate into an amorphous precipitate, or "gel," and the practically pure solvent. While crystalloid solutions are optically homogeneous, all colloid sols exhibit, in a greater or less degree, the "Tyndall effect" of scattering and polarising light, and, in most, minute suspended particles may be detected by the ultramicroscope. The relation of colloid sols to mechanical suspensions of very finely divided solids and to emulsions of immiscible liquids is a very close one, and may depend merely on the size of the particles. Many sols are visibly opalescent, but those with very small particles may be perfectly transparent, and metallic sols are often deeply coloured; gold sols vary from deep red to bluish violet.

The organic colloid sols differ in many respects from the inorganic, often approaching very closely to true solutions; and being usually bodies of high molecular weight and little subject to electrolytic dissociation, their true solutions would necessarily possess many of the properties associated with colloids. It is in fact by no means impossible that very large molecules or molecular aggregates may disperse and polarise light, and may even be made visible by the ultra-microscope. Organic sols are usually more stable than inorganic, and are flocculated or precipitated by different causes, so that it will be appropriate to defer their consideration till after that of the simpler and better investigated inorganic, or, as they are sometimes called, "suspension" colloids.

Inorganic colloid sols are invariably suspensions of very finely divided substances in media in which they are extremely insoluble. Von Weimarn ("Z. Chem. u. Ind. d. Kolloide," 1907, ii., p. 76) has shown that even the most definitely crystalloid bodies may be obtained in colloidal or gelatinised solution if produced in solutions in which they are extremely insoluble. An ordinary precipitate, such as barium sulphate, is at first formed by the combination of the ions in very minute crystal elements which are sufficiently soluble in water to rapidly unite to form crystals, which gradually increase in size by absorbing the smaller crystal elements. It is well known in ordinary analytical work that such precipitates will pass at first through any filter, but gradually become filterable by the effect of time and warmth. If, however, their insolubility is sufficiently increased by large excess of a common ion, or by effecting the combination in a medium, such as methyl alcohol, in which sulphates are extremely insoluble, the molecules cannot coalesce in the crystalline form, and a colloidal sol results. Even sodium and potassium chlorides have been obtained in colloidal form by the double decomposition of their organic compounds in organic media in which the salts were sufficiently insoluble. Though inorganic sols are precipitated by the addition of an electrolyte, the presence of free dissociated ions in small quantity seems essential to their formation and existence. If a solution of ferric chloride be dialysed through a colloid membrane into water, the hydrochloric acid formed by hydrolysis passes out into the water, leaving the ferric oxide in the dialyser as a colloid sol, and this goes on till the sol is practically free from chlorine, but if absolutely the last traces are removed, the ferric oxide flocculates and precipitates. Conversely, many oxide or hydroxide sols may be obtained by washing the precipitated hydroxide sufficiently free from electrolytes, or the precipitated and washed hydroxide may be re-dissolved by boiling with a very small quantity of neutral salt or free acid, when the precipitate will gradually pass into colloidal solution. This process (peptisation, Anätzung) has been extended to the colloidal solution of mechanically finely powdered oxides by the agency of small quantities of acids or salts, and has been employed by Kuzel (*D. R. P. Ammeld, 12g. K.* 30900 of Dec. 12, 1905) to bring many metallic oxides into the plastic condition requisite for the formation of the so-called "colloid" electric lamp filaments, now rapidly superseding the carbon fibre. Colloid sols are frequently formed by the free dilution of salts liable to hydrolytic dissociation, and especially salts of weak organic acids which from their low electrolytic dissociation do not readily cause precipitation. Even ferric chloride at a dilution of 1 : 125000 is completely dissociated in the cold in twenty-four hours, and much stronger solutions suffer partial dissociation, especially on heating. This is the cause of the darkened colour of hot ferric solutions. Acetates are still more readily hydrolysed, and especially by boiling, by which the free acetic acid is volatilised. Many solutions of hydroxides in alkalis are colloidal, but those in ammonia are usually true complex salts. Colloidal solutions are obtained of sulphides of metals of which the oxides, like those of arsenic and antimony, are soluble in water, by precipitation with H_2S, only water and the sulphide being formed in the reaction; and metallic sols of gold, silver, platinum, and other noble metals are formed by reduction of their dilute solutions, especially with organic reducing agents. Many sols may also be made by precipitation in presence of organic "protective colloids" which prevent precipitation by electrolytes. Thus silver halides may be obtained in colloidal solution in presence of gelatin, a fact of great importance in photographic plate making. An interesting point is that in many cases the nature of a sol may be changed by oxidadation, reduction, or chemical substitution without destroying its colloidal character.

An important method of producing metallic sols is that of Bredig (*Zeit. Angew. Chem.*, 1898, 951; *Zeit. Elektr.*, 1898, iv., 514), which differs in many respects from those just described. He employs the metal as cathode of an electric arc formed under water, which forms a sol with the particles projected from the cathode. Svedberg (*Ber.*, 1905, xxxviii., 3616) has applied the same method to the production of sols in ether, isobutyl alcohol, and other organic liquids, and of carbon, silicon, sulphur, and phosphorus in water (*Ber.*, 1906, xxxix., 1713). Bredig and Haber (*Ber.*, 1898, xxxi., 1741) have also shown that

under certain conditions sols can be produced by electrolysis, especially in alkaline solution.

The ultra-microscopes of Siedentopf and Zsigmondy ("Zur Erkenntniss der Kolloide," Jena, 1905) has rendered many details of colloid sols accessible to direct observation. In its original and most complete form it consists of a rectangular cell on the stage of the microscope, through the side of which a powerful horizontal beam of light is concentrated by appropriate lenses and adjustable slots; but several other types have been constructed for special purposes. No light can reach the observer but that from the brilliantly illuminated particles, which are thus rendered visible irrespective of size, as stars are visible to the naked eye on which the most powerful telescope can raise no measurable disc. As the field of view and the vertical thickness of the beam can be accurately measured, it is possible to count the visible particles in a given volume of liquid, and as the total concentration is known, their weight (and on certain assumptions as to form, their size), can be calculated. While the diameter of the smallest particles which could be seen by ordinary illumination, even with a magnifying power of 2250 diameters, is about 140 $\mu\mu$ (mm. $\times 10^{-6}$), Zsigmondy has observed particles in gold sols of from 20 to 80 $\mu\mu$ (submicrons), while still smaller particles (amicrons) exist, which scatter and polarise light, but cannot be separately distinguished. Zsigmondy estimates the size of the smaller of these amicrons as from 1·7 to 3 $\mu\mu$ (0·0000017 to 0·000003 mm.). Ostwald (Grundriss, p. 82) gives the probable size of a hydrogen molecule of molecular weight 2 as about 0·16 $\mu\mu$. As organic substances certainly exist having a molecular weight of several thousand, it seems quite probable that some of them may be visible to the ultra-microscope. Vanim and Hartl (*Ber.*, 1906, xxxix., 1696) have shown that if a small quantity of a ready-formed gold sol be added to a solution of a gold salt and a reducing agent, the colloid particles act as nuclei for the reducing gold. It is thus possible to build up amicrons to sub-microns which can be seen and counted. Some similar action takes place in gold ruby glass, which has been shown by Zsigmondy to owe its colour to colloid gold particles, but which is sometimes colourless until, by reheating, the gold germs have been allowed to grow by absorbing amicrons or reducing gold salts.

Other metallic and inorganic sols appear to contain particles of the same order of magnitude as the gold sols, but different sols vary considerably, and any sol contains a mixture of particles of various sizes.

As seen by the ultra-microscope, the particles are not at rest, but in constant rapid vibrating movement, and, according to Zsigmondy, gold particles have also a translatory motion. This vibration, which certainly plays its part in the physics of colloid sols, is identical with the Brownian or pedetic motion common to all minute particles suspended in liquid, but more marked in the ultra-microscopic, since it increases inversely with the size of the particles. This motion increases with temperature and diminishes with increased viscosity of the liquid, but is permanent and unaffected by time, or apparently by the exclusion of radiant heat and light. All theories therefore which ascribe the energy involved to outside influences would seem to be excluded, but it must be remarked that it is impossible to *observe* the phenomenon without light, and, ultra-microscopically, without light of a very intense character, so that the view suggested by Regnauld (*Journ. d. Pharm.*, [3], 1857, xxxiv., 141), that it was due to the warming of the particles by radiant heat, cannot perhaps even yet be entirely ignored. Sir W. Ramsay (CHEMICAL NEWS, 1892, lxv., 90) suggested that the motion was directly due to the heat-vibration of the water-molecules, though he thought it necessary to assume highly complex water-molecules to account for the disturbance of the much heavier solid particles. Einstein (*Ann. Phys.*, [4], 1905, xvii., 549, and 1906, xix., 2) and Smoluchowski (*Ann. Phys.* [4], 1906, xvii., 756) have discussed the phenomenon mathematically from two entirely different physical standpoints, and have reached results which not only show a scarcely expected concordance with each other, but a close relation to observed facts. The experimental work of Svedberg (*Ark. för Kemi, Min. och Geol.*, 1907, ii., *Nr.* 34) also strongly supports this view, so that, without presuming to discuss the mathematical evidence, it appears that a strong case is made out for regarding the motion as a direct consequence and evidence of the kinetic theory of heat. It may be remarked that if external sources of energy can be excluded, heat-motion seems the only available cause, since all the energy involved in overcoming internal friction of the liquid is converted into diffused heat, which in a space of uniform temperature cannot be re-transformed into any other form of energy.

If an electric current of sufficient strength be passed through an aqueous electrolysable solution in which the anode and cathode are separated by a diaphragm of porous earthenware, the liquid will pass through the latter towards the cathode till a certain equilibrium pressure is established. The phenomenon is known as "electrical osmose" or "cataphoresis." Although observed by Reuss in 1809, the subject was first systematically investigated by Wiedemann (*Ann. Phys.*, [2], 1852, lxxxvii., 321; and "Die Lehre der Elektrizität," 1893, Bd. I., 993). He showed that, with uniform difference of pressure, the quantity of liquid which passed through the diaphragm was proportional to the current-strength and independent of the area or thickness of the porous plate; and the pressure attained, when equilibrium was reached, to the potential difference between the two sides of the diaphragm. Quincke (*Ann. Phys.*, 2], 1861, cxiii., 513), substituting a capillary tube for the diaphragm, confimed these laws, and showed further that the equilibrium-pressure increased with diminished bore and relatively increased surface of the capillary; and that not only the pressure, but the direction of the flow were dependent on the nature of the material of the capillary and the liquid employed; oil of turpentine flowing to the anode in a glass capillary, and in the reverse direction in one lined with sulphur. It is obvious, therefore, that the action is between the surface of the liquid carrying the electric current and that of the capillary, and that if the liquid were fixed and the capillary surface free to move, it would be carried in the opposite direction to the flow of the liquid. This will be the case with suspended particles; and it has long been observed that these are carried in one or other direction according to their material and that of the liquid, most substances moving toward the anode in water and the cathode in turpentine, with a velocity proportional to the current-strength, but independent of their distance from each other and of the electromotive force. Quincke assumed that the particles possessed electrical charges different from the liquid, and usually negative as compared to aqueous solutions; so that in a current the particle would tend to move to a region of higher + potential; that is, towards the anode. The relation of these facts to the contact-theory and to the phenomena of frictional electricity is obvious; a stream of liquid forced through a capillary of different potential would necessarily give rise to an electric current if furnished with appropriate conductors.

Helmholtz supported and somewhat amplified the hypothesis of Quincke (*Ann. Phys.*, [3], 1879, vii., 337). According to him, the limiting surfaces of two bodies of opposite electric character form a "double layer" (Doppelschicht); the + charge of the one layer exactly equalling the − charge of the other, and thus exerting no outside effect. Under the influence of a fall of potential the liquid layer tends to move over the other, and by friction communicates its motion to the adjacent liquid. Billitzer (*Wien. Ber.*, 1903, cxii., 95) supposes that the liquid coating of the double layer communicates its charge by diffusion to the remainder of the liquid, and, as this charge is constantly renewed by contact-action, both liquid and particles assume permanent charges, so that the latter behave, in a certain sense, like free ions. It is possible, or

perhaps probable, that the particles owe their original charges to the actual attachment of free ions by their residual affinities. It is not necessary to suppose, or even probable, that when two or more atoms unite to form a molecule their affinities are quantitatively saturated, but merely that, under the conditions, the residual affinity is insufficient to attach another atom. Under these circumstances it is likely that a mass of molecules may be able to hold additional ions in a way probably identical with what is known as "adsorption"; and these ions will affect the charge of the mass. The bearing of this on the phenomena of flocculation will be referred to later.

(To be continued).

DYNAMIC ISOMERISM.*

A.

Since the appearance of the last Report the experiments on the influence of acids, bases, and salts in accelerating isomeric change in solutions of nitrocamphor have been completed and published (Lowry and Magson, "The Influence of Nitrocamphor on the Mutarotation of Nitrocamphor," *Trans. Chem Soc.*, 1908, xciii., 107).

B.—Carbonyl Chloride as an Agent for Arresting Isomeric Change.

The most important feature of the year's work has been the discovery of a group of agents by means of which the isomeric change of nitrocamphor can be retarded or completely arrested. As long ago as 1899 (Lowry, *Trans. Chem. Soc.*, 1899, lxxv., 211) it was observed that solutions of nitrocamphor in chloroform behaved in an abnormal manner in that isomeric change was sometimes arrested during a period of one or two weeks and then abruptly started by some slight change of conditions, *e.g.*, by transferring the solution from a flask to a polarimeter tube.

The abnormal properties of this solvent were again noticed in the recent experiments on the influence of acids and bases. The basic chloroform solutions showed a marked decrease of activity when kept for a few days, whilst dilution produced a loss of catalytic power out of all proportion to the decreased concentration of the base. In one extreme case the isomeric change in a solution to which a trace of piperidine had been added practically ceased at the end of a fortnight, although the final condition of equilibrium had not by any means been reached. The more concentrated acid solutions produced an acceleration of isomeric change, but a retardation was noticed when smaller concentrations were used; in one case the rotatory power of the solution remained absolutely constant during a period of twenty-four days.

The earliest observations of arrested isomeric change had led to the conclusion that in non-oxygenated solvents the change was conditioned by the presence of a third substance, probably a basic impurity. The retardation produced by the acid chloroform solutions could not be attributed to mere neutralisation, since an acceleration was observed when benzene was used as the solvent. It was noticed, however, that the chloroform solutions acquired a pungent and unpleasant odour, which was ultimately traced to the formation of carbonyl chloride by oxidation of the chloroform $CHCl_3+O=COCl_2+HCl$; to this substance the curious behaviour of the chloroform solutions was undoubtedly due.

The action of the chloride probably depends on its power of converting ammonia and bases such as piperidine into neutral carbamides—

$$COCl_2+2NH_3=2HCl\cdot CO(NH_2)_2,$$
$$COCl_2+2NC_5H_{11}=2HCl+CO(NC_5H_{10})_2.$$

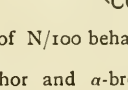
It was found that the chloride was capable of retarding or arresting the isomeric change of nitrocamphor dissolved in benzene or in ether, and that acetyl chloride produced a similar effect in benzene and in carbon disulphide. Phenylcarbamide did not retard the isomeric change of nitrocamphor dissolved in benzene, and acetyl chloride proved inefficient when added to a solution in acetic acid. In the latter case it is probable that the solvent has itself a catalytic action, and this may also be true when water and alcohol are used. The bearing of these observations on the problem of chemical change has been discussed elsewhere (*Trans. Chem. Soc.*, 1908, xciii., 119).

C.—Relationship between Absorption Spectra and Isomeric Change.

As the result of a series of experiments on the absorption spectra of substances of the ethyl aceto-acetate group, Baly and Desch (*Ibid.*, 1904, lxxxv., 1029; 1905, lxxxvii., 766) were led to the conclusion that there was a close relationship between the absorption bands which appeared in the spectra of some of these compounds and the property which they possess of undergoing reversible isomeric change. In view of the importance of this hypothesis in relation to the subject of dynamic isomerism it was thought to be desirable to test it in the case of a number of optically active compounds. These have the advantage that many of them can be crystallised out in a pure enolic or in a pure ketonic form, that it is possible by means of polarimetric observations to determine the actual velocity with which they undergo isomeric change, and that in a number of cases the proportions in which the isomerides are in equilibrium can be determined by means of solubility measurements. Photographs have therefore been taken of the absorption spectra of the majority of the camphor-derivatives which have formed the subject of previous investigations, and we are now in a position to summarise the principal results that have been obtained.

Halogen-derivatives of Camphor.

1. The camphor band observed by Baly and by Hartley at a concentration of N/10 practically disappears when the concentration of the alcoholic solution is reduced to N/100 (thickness of liquid 250 to 2·5 mm.), but can be restored by the addition of alkali. β-Bromocamphor,—



at a concentration of N/100 behaves in the same way as camphor.

2. α-Chlorocamphor and α-bromocamphor at a concentration of N/100 show a band in the same position $\left(\frac{1}{\lambda}\ 3400\right)$ as the camphor band. The band is eliminated when the second α-position is occupied by bromine or by a nitro-group, but remains unaffected when the halogen is introduced in the β- or in the π-position.

3. No marked change in persistence is produced by the addition of alkali to α-chlorocamphor, α-bromocamphor, or their β- and π-bromo-derivatives. All these compounds are quite stable when alone, but undergo isomeric change rapidly in presence of a small proportion of alkali. It is therefore evident that in this case at least there is no direct quantitative relationship between the velocity of isomeric change and the persistence of the absorption-band.

Nitro-derivatives.

4. Nitrocamphane shows no absorption band, whether the solution be prepared by dissolving the crystals of the normal form or by adding acid to the sodium salt of the pseudo form. Even in presence of ten equivalents of alkali no definite band is developed. It is therefore clear that dynamic isomerism, even of a well-pronounced type, is not necessarily associated with the production of a band.

* Report of the Committee, consisting of Professor H. E. Armstrong (Chairman), Dr. T. M. Lowry (Secretary), Professor Sydney Young, Dr. C. H. Desch, Dr. J. J. Dobbie, Dr. M. O. Forster, and Dr. A. Lapworth. (Drawn up by the Secretary). Read before the British Association (Section B), Dublin Meeting, 1908.

5. Nitrocamphor dissolved in alcohol shows a shallow band at $\frac{1}{\lambda}$ 3000; it differs in position from that produced by bromocamphor—a result that is in accord with the view, consistently advocated, that the mobile hydrogen atom in this compound wanders to the nitro and not to the carbonyl group. The band disappears in the α-chloro and α-bromo derivatives, and also in the anhydride derived from the pseudo form by loss of water; its occurrence appears therefore to be limited by the same conditions as those which determine the occurrence of isomeric change.

6. In marked contrast with the behaviour of the —CHX.CO— compounds described above, the nitrocamphor band is enormously intensified by the addition of alkalis. This result is, perhaps, associated in some way with the fact that nitrocamphor forms a stable sodium salt whilst bromocamphor does not.

7. Camphoryl oxime—the isomer of nitrocamphor—resembles it in giving a very intense band in presence of alkalis, although the head of the band occurs at a considerably smaller wave-length $\left(\frac{1}{\lambda}\ 3650\right)$. The band does not appear in solutions of the oxime alone, and is not given by the acetyl derivative. Camphoric adhydride, the parent-substance from which the oxime is derived, is very diactinic, and shows no band.

Sulphonic-derivatives of Camphor.

8. β- and π-sulphonic derivatives containing the group—

$$Y.SO_2.C_8H_{13}\begin{cases}CHX\\ |\\ CO\end{cases}$$

usually show an absorption band, but this does not appear in camphor-β-sulphonamide and some of its derivatives. The replacement of both α-hydrogen atoms by halogens causes the band to disappear.

D.—CAMPHORCARBOXYLIC ACID.

Investigations of the mutarotation phenomena and absorption spectra of camphorcarboxylic acid and its derivatives are in progress, but as the work is not yet complete it is proposed to reserve the discussion for a subsequent report.

THE FORMATION OF MISTS IN PRESENCE OF RADIUM EMANATION.

By Mdme. CURIE.

IN a previous article I showed that the presence of radium emanation causes the condensation of saturant or non-saturant water vapour, as well as of other vapours. This condensation is manifested by the formation of a persistent mist, visible by the light of an electric arc (*Comptes Rendus*, December, 1907).

I have shown that the centres of condensation can neither be the ions formed in the gas nor the molecules of the emanation. It might be supposed that they are the particles of induced radio-activity suspended in the gas acting either by the electrostatic attraction of their charge, or by chemical affinity. It might also be thought that under the action of the emanation chemical compounds, capable of absorbing the vapour until drops are formed, arise in the gas. The second opinion is confirmed by experience, and experiments performed with water vapour are very conclusive on this point.

The experiments were carried out in sealed 150 cc. glass bulbs containing the liquid or solid to be investigated, and the gas charged with emanation (air, carbon dioxide, or hydrogen). To take an observation each bulb was placed in a water-bath and lighted by a convergent beam of light issuing from an electric arc. The quantity of emanation was approximately the same in the different experiments; it was the limiting quantity which can be emitted by 0·03 grm. of radium chloride. Blank experiments were performed with bulbs which did not contain the emanation. The mists due to the emanation are persistent, and can easily be distinguished from those which are produced by inequalities of temperature. They may last more than a month, and they disappear gradually in consequence of a gradual diminution in the number of drops as the emanation decays.

With pure water and air charged with emanation a persistent mist is observed; this mist is always slight, and it lasts some days. If the air is replaced by carbon dioxide no persistent mist is observed. But if, instead of using pure water, a mixture of equal weights of water and sulphuric acid is used, a dense mist, which is generally very fine at first, is obtained both in presence of air and of carbon dioxide; this mist can be observed for more than a month. The formation of mist is thus much facilitated by the addition of sulphuric acid to the water, when the pressure of the water vapour is greatly decreased.

In these experiments the particles of induced radio-activity cannot act directly as centres of condensation, for these particles exist in carbon dioxide as well as in air; moreover, their action would become more energetic with saturant than with non-saturant water vapour. It is natural to suppose that if we are dealing with water and air the centres of condensation are the nitrated compounds formed in air in presence of the emanation. If the mixture of sulphuric acid and water is used we are led to the supposition, though it may appear strange, that particles of sulphuric anhydride are formed in the gas owing to the action of the emanation on the liquid. A very persistent mist is also obtained in a flask which contains concentrated sulphuric acid and emanation in carbon dioxide; this mist lasts more than a month, while the much more intense mists which can be produced in another flask by local heating last less than a day.

Various experiments have been performed to demonstrate the *rôle* of chemical reactions.

If a flask which contains water and air charged with emanation is not sealed up but closed with a rubber cork, the mist obtained is much more dense and lasts much longer. It might be supposed that in this case the formation of centres of condensation results from chemical action on the cork, with oxidation of the organic matter and the sulphur. This supposition is confirmed by the following experiment:—A sealed glass bulb contains water, air charged with emanation, and a glass rod, on which is a piece of fused sulphur, and which is not immersed in the water. A fine mist appears in the flask and lasts for a month; after the experiment traces of sulphuric acid can be detected in the water.

Mists which are very intense at first and last more than a month have been observed with petroleum ether and carbon disulphide in presence of air charged with emanation; in the second case, the change in the liquid is very rapid, as shown by the formation of brown membranes. Anhydrous ether in presence of carbon dioxide and emanation also gives a persistent mist. In all cases probably the organic substances are attacked.

I have also examined certain solid substances, and I have obtained dense mists of long duration by using iodine in carbon dioxide charged with emanation, and camphor in air charged with emanation. On the other hand, if iodine is used with air and emanation, the mist only lasts for some days. During the dense mist visible deposits are produced on the walls of these flasks which do not contain liquid.

A mist may be observed with actinium in presence of water and carbon dioxide.

I have examined the action of an electric field on the mist formed in presence of the emanation. For this purpose I used a litre flask in which there were two parallel plates forming electrodes. The mist was obtained by means of a mixture of water and sulphuric acid; the volume being large it was necessary to use much more emanation than

before. I have proved that, as a whole, the drops behave as if they were not charged. It is true that they are violently attracted towards the electrodes, so that the mist rapidly disappears; nevertheless, this is only an effect of the displacement of uncharged particles in a field which is not uniform; the attraction acts towards the edges of the two electrodes, and the appearance of the displacement is independent of the sense of the field.

The formation of mist in a vessel which contains emanation may be regarded as an index of chemical reaction. Some experiments have been performed in my laboratory by M. Hirszfinkiel to determine the products of the reactions which may have occurred in the flasks used for my experiments. The most definite results were as follows:—Formation of a little carbon monoxide from the dioxide (a reaction already observed by Ramsay and Cameron), formation of nitrated compounds in the air, formation of traces of sulphuric and sulphurous acids in presence of sulphur and air.

M. Barkow has recently studied the condensation of water vapour under the influence of the Röntgen rays, of ultra-violet light, and of the penetrating radiation of radium. He frequently obtained condensation with slight expansion and attributed it to the formation in the gas of certain chemical compounds, such as nitrated compounds (*Ann. d. Physik.*, 1907).

The mists which I observe are composed of fine mobile drops, which are carried along by slow movements produced in the middle of the gas. When such a mist is not visible it often appears as if a much finer mist could be seen in the flasks which contain the emanation, although their existence could not be demonstrated with certainty.

The emanation must be fairly concentrated at first in order to produce the mist, which, however, may persist for a month when the concentration of the emanation has been reduced about 200 times.—*Comptes Rendus*, 1908, cxlvii., 379.

ACTION OF RADIUM EMANATION ON SOLUTIONS OF COPPER SALTS.

By Mdme. CURIE and Mdlle. GLEDITSCH.

A year ago Ramsay and Cameron announced in various publications that they had observed the production of alkali metals and of lithium in solutions of copper salts which had been subjected to the action emanation. They concluded that, in presence of the emanation, the metal copper undergoes a degradation into elements of the same family of lower atomic weight—potassium, sodium, lithium (*Nature*, July, 1907; *Journ. Chem. Soc.*, September, 1907; *Comptes Rendus*, 1908; *Archives de Genèvre*, April, 1908).

These important results attracted much attention, and it seemed desirable to reproduce them in laboratories which possess a sufficient amount of radium.

The experiment was performed as follows:—A solution of a copper salt (sulphate or nitrate) was placed in a little glass flask into which a large quantity of emanation was introduced and allowed to decay there spontaneously. The copper was then separated, the remaining solution evaporated to dryness, and the residue examined. The same operations were carried out with a solution of the same copper salt which had not been subjected to the action of the emanation. The experiments were repeated several times. The residue consisted chiefly of a sodium salt (with a little K and Ca); in the four experiments described, in which the emanation had been used, the presence of lithium was observed by means of a spectroscope. In the blank experiments the residue was much smaller, and no lithium could be detected. Ramsay and Cameron performed an experiment to determine the amount of lithium present; they found about 0·00017 mgrm. of lithium in a residue which weighed 1·67 mgrm. obtained from 0·27 grm. of copper (0·815 grm. of copper nitrate), while in the corresponding blank experiment the residue was only 0·79 mgrm. (This weight of metallic lithium does not correspond to the amount indicated by the mixture of sodium and lithium salts used for comparison, and there must have been an error which we have not been able to detect).

We tried to repeat the experiment, taking every possible precaution. The experiment is delicate, and is liable to be affected by many sources of error, the chief of which is the use of a glass vessel, as Ramsay himself has stated.

Our preliminary experiments have shown that it is extremely difficult to get chemical products free from lithium.

It is found in distilled water and in almost all reagents; if a reagent does not contain it, and is allowed to remain some time in a glass vessel, it is then found to contain some traces of the element. The following experiment was performed:—Water which had been distilled in a platinum still and kept in a platinum flask, left no visible residue when 250 cc. were evaporated in a platinum dish, and the last drop formed by the concentration process did not give the lithium spectrum. But if water obtained in the same way is kept in a glass flask for twenty-four hours, after evaporation a small residue is obtained, consisting chiefly of a sodium salt, but containing also a trace of lithium.

It seemed to us indispensable to replace the glass by some other substance. We have proved that it is equally dangerous to use quartz, a substance which was employed by Ramsay, for commercial quartz vessels contain lithium. We treated the fragments of a dish of opaque quartz and a piece of a transparent quartz tube with hydrofluoric acid free from lithium; a considerable amount of lithium could be detected in the residue. Transparent quartz contains much more than opaque quartz. We therefore decided to use platinum vessels.

The apparatus we used consisted of a cylindrical platinum receiver 7·5 cm. long and with an external diameter of 1·5 cm. placed horizontally; at the end of this receiver there was a little vertical platinum tube through which we introduced the solution. The little tube had a platinum lid, which protected the solution, but did not act as an air-tight stopper. A glass tube was soldered externally over the platinum tube; it was furnished with a side tube with a stopcock. The solution was introduced into the apparatus by means of a platinum syphon, and was withdrawn in the same way, and was never allowed to come in contact with the glass parts of the apparatus.

The water and the acids used for the experiment were re-distilled in a platinum still, and kept in platinum bottles. We found that all the reagents contained lithium, especially the sulphuric acid. After the purification process the presence of lithium could not be detected in the residue from the evaporation of 80 cc. of nitric acid, 25 cc. of sulphuric acid, 25 cc. of hydrofluoric acid, and 250 cc. of water.

As Ramsay had observed, commercial pure copper salts contain considerable amounts of lithium.

We tried various methods of purification—repeated precipitation with sulphuretted hydrogen, deposition of copper by electrolysis, fractional crystallisation; we finally used copper sulphate which had been subjected to many crystallisations in a platinum dish, pure water being always used for re-dissolving. At first this treatment is very efficacious, but it is very difficult, if not impossible, to remove the last traces of lithium. After the purification had been performed, it was possible with difficulty to detect lithium in the residue from the treatment of 50 grms. of copper, but none could be detected in the residue from 2 grms. of salt.

The emanation was obtained from a solution which contained 0·19 grm. of radium (0·25 grm. $RaCl_2$). It was first condensed in a worm immersed in liquid air, and then drawn into the apparatus. In order that the quantity of emanation used might be known exactly we measured the radiation emitted from the apparatus by comparison with that of a known amount of radium. For the measurement a specially constructed condenser with large plates was used.

Two experiments analogous in every respect were performed. About 7 cc. of a solution of pure copper sulphate were introduced into the apparatus; this liquid presented a large free surface relative to its volume. The emanation was introduced by degrees, and in order to make sure that it dissolved, the solution was shaken by inclining the apparatus, which was placed in melting ice. This process was repeated several times. The weights of metallic copper employed were 0·26 and 0·14 grm. The whole quantity of emanation introduced was in both cases measured by the saturated emanation of 0·37 grm. of radium; the quantity of emanation which was actually destroyed in the apparatus was rather less; it was measured by the saturated emanation of 0·27 grm. of radium. When the experiment was thought to be finished the solution was transferred from the apparatus into a platinum dish, and some drops of nitric acid were added. A platinum electrode was introduced into the same dish, and the copper was deposited on it. The solution after being freed from copper was evaporated to dryness in the dish, and heated until the sulphuric acid was driven off. The residue was dissolved in a few drops of water, and treated with sulphuretted hydrogen to remove the traces of copper still present. The liquid was filtered through a little platinum funnel on to a platinum lid of known weight, and evaporated to dryness at a very moderate temperature. The very small residue obtained was weighed.

Seven cc. of a solution of pure copper sulphate which had not been exposed to the action of the emanation was subjected to the same treatment. The residues finally obtained were examined with a spectroscope. Their weights were 0·0004 and 0·0005 grm. in the first experiments, and 0·0003 and 0·0002 grm. in the blank experiments.

It must be noted that the amount of copper used is about the same as that employed by Ramsay. The quantity of emanation used is also approximately the same (1·85 cmm. of emanation according to Ramsay's method of estimation). Nevertheless, the residue finally obtained is much smaller.

The spectroscopic examination showed that this residue contains principally sodium and a little potassium; the presence of lithium could not be proved. An experiment performed with mixtures of sodium and lithium sulphates showed that it is possible, though with difficulty, to detect the presence of the red lithium line with a mixture which contains 1 part of Li_2SO_4 in 10,000 parts of Na_2SO_4, and that it is easy to see the same line with a mixture containing 1 part of Li_2SO_4 in 3000 parts of Na_2SO_4. Consequently, the quantity of metallic lithium which could be present was less than $0{\cdot}6 \times 10^{-5}$ mgrm.

With the same amounts of copper and of emanation, Ramsay and Cameron state that $1{\cdot}7 \times 10^{-4}$ mgrm. of lithium was present. If, owing to a clerical error, this number represents lithium chloride, the amount of metallic lithium would be 3×10^{-5} mgrm.

The residue which we obtain is always much less than that obtained by Ramsay and Cameron, and this is probably due to the rejection of glass vessels. The difference in the weights of the residues obtained by us in the direct and in the blank experiments is very small (0·1 to 0·3 mgrm.); this is probably because in the experiment performed with the emanation the entrance of the latter might lead to the introduction of traces of foreign matter. In Ramsay and Cameron's most complete experiment this same difference was 0·88 mgrm., and we think that it might be attributed to the more energetic attack upon the glass by the solution in presence of the emanation.

The following control experiment was performed:—Into a solution of copper sulphate containing 0·27 grm. of copper we introduced the amount of lithium sulphate corresponding to $1{\cdot}7 \times 10^{-4}$ mgrm. of LiCl; this solution was then treated in the same way as in the experiments described above. With the residue finally obtained it was easy to see the red lithium line, which proves that the lithium was not lost during the treatment.

Thus, we may say that we have not succeeded in confirming Ramsay and Cameron's experiments. It is evidently impossible to assert that no trace of sodium or lithium is formed in the experiment, but we consider that the formation of these elements cannot be regarded as proved.—*Comptes Rendus*, 1908, cxlvii., 345.

THE ELECTROLYTIC PROPERTIES OF DILUTE SOLUTIONS OF SULPHURIC ACID.*

By W. C. D. WHETHAM, M.A. F.R.S., and H. H. PAINE, B.A., Trinity College, Cambridge.

(Continued from p. 130).

PART II.—*By* H. H. PAINE (*continued*).

8. *The Conductivity Curve.*

WE are thus led to consider once more the cause of the drop in the equivalent conductivity curve. The evidence seems conclusive against the supposition that the presence of carbonic acid, or indeed of any other acid, is sufficient to explain the phenomenon.

In the same series of experiments as those with exhausted water, referred to in the first part of the paper, the effect of the presence of carbonic acid deliberately introduced into the solution was ascertained (*Roy. Soc. Proc.*, A, lxxvi., 580). If instead of plotting the k/m curve as was there done, we plot the total conductivity of the solution against the concentration of sulphuric acid—both for the solution containing carbonic acid and that made up from the pure distilled water—we shall find that the curve for the former case always lies above that for the latter, the two gradually merging as the concentration increases. The difference between the ordinates of the two curves at any particular concentration gives us the effect of the carbonic acid on the conductivity. The effect is always positive, but diminishes in magnitude as the concentration of the sulphuric acid increases. This is explained simply and logically on the supposition that the carbonic acid behaves as a "second acid," contributing its partial conductivity to the whole conductivity of the solution. Since it is a very weak acid, its ionisation is suppressed by the hydrogen ions of the sulphuric acid, and hence its effect will become less and less, ultimately becoming negligible, as the concentration of the sulphuric acid increases. Hence, by subtracting the full initial conductivity of the solvent containing carbonic acid, we make the partial conductivity of the sulphuric acid appear smaller than it really is, and thus apparently get a drop in the k/m curve. If the purest distilled water contained carbonic acid, the presence of this impurity would explain part of the drop observed, but there remains an excess effect to be accounted for in another way.

For let us consider the equivalent conductivity curve for a solution made up with the purest water obtained by distillation in air. If, instead of deducting the conductivity of the solvent, we take the total conductivity of the solution in plotting the k/m curve, we shall find that the curve still falls off at extreme dilutions. Since the effect of carbonic acid is always additive, correcting for it, to get the true conductivity of the sulphuric acid, can only exaggerate the drop in this curve. Hence on the basis of any known phenomenon, the presence of carbonic acid, or of any other free acid, is insufficient to explain the whole of the apparent diminution in the conductivity of the sulphuric acid.

Water distilled *in vacuo* has a much smaller conductivity than that distilled in air; hence most of the impurities in the latter are dissolved from the air. Now the atmospheric gases most likely to be dissolved in any appreciable quantity are carbonic acid and ammonia. Normally there is forty times as much carbonic acid as ammonia in the atmosphere, but the solubility of ammonia is so much greater than that of carbonic acid that the quantities of each which would be

* A Paper read before the Royal Society, June 18, 1908.

present in solution are probably of one and the same order.

Let us then regard the solvent as containing ammonium carbonate, which at such dilution would be largely in the ionised state. The addition of a strong acid will result in the formation of un-ionised carbonic acid—the ammonium ions remaining in solution. Some of the hydrogen ions of the strong acid have thus been removed. We may regard the first small quantity of acid added as being removed from the solution or rendered inactive, and the partial conductivity as due to the portion left.

Again, instead of adding an acid, let us introduce a strong alkali like potash. Here we shall have un-ionised ammonia (or ammonium hydrate) formed, and some of the hydroxyl ions of the strong alkali will be removed from the solution. As before, the effect is the same as though the first portion of alkali added had been nullified.

This view is best made evident from the conductivity curve—plotting the "partial conductivity" of the acid (the conductivity of the solution minus the initial conductivity of the solvent) against the mass of acid added. A quantitative as well as a qualitative agreement with facts may be observed. The curve is a straight line. When produced it does not pass through the origin, but cuts the axis of zero conductivity at a point showing the concentration of acid to be $4{\cdot}7 \times 10^{-6}$ grm.-equivalent per litre (for a curve plotted during the course of the experiments described in this paper). The effect on the conductivity therefore is the same as though this quantity of acid had been neutralised or removed from solution. Now from the migration constant experiments, since the rise in the measured migration constant was only half what we should expect if the whole of the conductivity of the solvent had been due to saline matter, we may conclude that about half this quantity of salt was present in the water, giving a conductivity of about 5×10^{-7}. Suppose this salt to be ammonium carbonate. The velocity of the CO_3 ion (deduced from the migration constants of potassium and sodium carbonates and sulphates) is about 50, while that of the (NH_4) ion (deduced in a similar manner from the figures for ammonium chloride, &c.) about 70. Hence $u + v = 120$. We then get $k = m(u + v) = 5 \times 10^{-7}$, so that $m = 5 \times 10^{-7}/120 = 4{\cdot}2 \times 10^{-9}$ grm.-equivalent per cubic centimetre, or $4{\cdot}2 \times 10^{-6}$ grm.-equivalent per litre.

If this be the quantity of ammonium carbonate present in solution, it would account for the neutralisation of an equivalent quantity of sulphuric acid. The agreement with the number deduced from the conductivity curve is very close indeed.

It was also noticed that, when exposed to the air, the conductivities of dilute solutions of acid diminished, often at a considerable rate. That no solution of alkali from the glass produced this effect was shown by preventing the air from getting into contact with the solution, when the conductivity remained quite constant. This seems to show that ammonia, or some other alkali, is readily absorbed from the atmosphere—the hydrogen ions being replaced by ammonium ions in the solution, and the total conductivity being diminished.

There is an objection which must be faced. A solution of ammonium carbonate, on boiling, gives off ammonia and carbonic acid. Hence, in the exhaustion experiments described in the first part of this paper, when the conductivity of the solvent was considerably reduced before the addition of the sulphuric acid, we might have expected that some of the ammonium carbonate would have been abstracted, and the effect made apparent on the k/m curve. It must be remembered, however, that the last traces of ammonia would be removed only with great difficulty. Further, from the above calculations it would appear probable that half the conductivity of the solvent is due to the presence of something which does not affect the transport ratio. If this represents an excess of carbonic acid, the results are explained. Since ammonia is much more soluble than carbonic acid, the latter would be evolved much more readily on exhausting the water. Hence the diminution in conductivity would be accounted for by the removal of the carbonic acid, while the ammonia present may be almost unaffected.

9. We have sought to explain the apparent diminution in the equivalent conductivity of acids (and similarly of alkalis) at extreme dilution, by the association of ions brought together in solution. Such as association would take place if the solvent contained :—(1) A weak acid such as carbonic acid, (2) a weak alkali such as ammonia, or (3) a salt formed by the neutralisation of a weak acid by a weak alkali, such as ammonium carbonate. We have seen that experimental evidence is opposed to the supposition that the presence of carbonic acid alone is sufficient to explain the phenomenon ; we have concluded that the presence of ammonium carbonate is capable of providing this explanation. It has been shown that the diminution in the equivalent conductivity would be accounted for if by some means the conductivity of $4{\cdot}7 \times 10^{-6}$ grm.-equivalent of sulphuric acid per litre were destroyed. Hence the "impurity" in the water must be such as will produce this electrical effect. Now consider the three cases. In the first, we should get approximately the same result electrically, if there were 5×10^{-6} grm.-equivalent of ionised carbonic acid per litre of the solvent, which becomes un-ionised on the addition of the strong acid ; in the second, $3{\cdot}5 \times 10^{-6}$ grm.-equivalent of ionised ammonia per litre would be sufficient ; and in the third, 5×10^{-6} grm.-equivalent per litre of ammonium carbonate—also in the ionised state. The conductivities of these solutions would be—

$$1.\ k_1 = 5 \times 10^{-9}(319 + 50) = 1{\cdot}8 \times 10^{-6},$$
$$2.\ k_2 = 3{\cdot}5 \times 10^{-9}(184 + 70) = 0{\cdot}9 \times 10^{-6},$$
$$3.\ k_3 = 5 \times 10^{-9}\ (70 + 50) = 0{\cdot}6 \times 10^{-6}.$$

The actual conductivity of the water was between $0{\cdot}9 \times 10^{-6}$ and $1{\cdot}0 \times 10^{-6}$. Hence there could not have been sufficient carbonic acid present in the free state in the distilled water to account for the observed "diminution" in the conductivity of the solution. The conductivity of the water easily allows for the presence of sufficient ammonium carbonate. The case for ammonia is just on the border-line. The high velocities of the hydrogen and hydroxyl ions make the number of grm.-equivalents of an acid or alkali required to produce a given conductivity, less than that of a salt. That is why, for a given conductivity, ammonium carbonate is more effective in reducing the conductivity of the solution of sulphuric acid than ammonia or carbonic acid present separately.

We have assumed throughout this final investigation that the velocities of the ions remain constant for the greatest dilutions. It is still possible that these velocities diminish, and that the above explanation only partially accounts for the drop in the k/m curve. To complete the solution of the problem, it would be necessary, either to obtain an exact knowledge of the impurities in the water, so as to allow for their effect, or to use water which contained no such impurities. In the water distilled in air, it is probable that ammonia and carbonic acid are dissolved ; if so, the effect in diminishing the conductivity necessarily follows.

The Staffordshire Society.—The Council of the above Society is making a special effort to increase the membership. It is well known there are many Staffordshire men in London and the provinces, most of whom would, no doubt, appreciate the objects of the Society, which are to promote social intercourse, cordiality, and good fellowship ; also to further objects of interest to the County. The Society offers excellent opportunities for bringing together friends from their own County. The Hon. Secretary of the Members' Committee, Mr. E. A. BARNETT, 2, Audley Road, Hendon, N.W., will be pleased to receive names and addresses of Staffordshire men who desire to become members of the Society.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

PART III.—ANALYSIS OF THE ALUMINIUM AND IRON GROUPS, INCLUDING BERYLLIUM, URANIUM, VANADIUM, TITANIUM, ZIRCONIUM, AND THALLIUM.

By ARTHUR A. NOYES, WILLIAM C. BRAY, and ELLWOOD B. SPEAR.

(Continued from p. 108).

The Iron Group (continued).

Procedure 65.—When phosphate is present, test one-tenth of the HNO_3 solution (P. 63) for iron, by evaporating it just to dryness, adding 1—2 cc. HCl (1·20), evaporating again to decompose the HNO_3, diluting to 5 or 10 cc. and adding 5 cc. KCNS solution. (Permanent red colour presence of *iron*). To the remainder of the solution add NH_4OH (0·96) until the precipitate formed by the last drop does not re-dissolve on shaking. If, owing to the addition of too much NH_4OH the solution becomes alkaline or a large precipitate separates, make it distinctly acid with acetic acid. Add 5 cc. of a 50 per cent solution of ammonium acetate, and, unless the mixture is already of a brownish red colour, add 10 per cent $FeCl_3$ solution drop by drop until such a colour is produced. Add enough water to make the volume about 100 cc., boil in a 250 cc. flask for five minutes, adding more water if a very large precipitate separates, and let the mixture stand for a minute or two. Filter while still hot, and wash with hot water. Add 3—5 cc. more ammonium acetate solution to the filtrate, boil it again, and collect on a separate filter any further precipitate. Make the filtrate alkaline with NH_4OH, adding an excess of 2—3 cc., filter off and wash any precipitate, uniting it with the main precipitate. (Filtrate, P. 66; precipitate, reject or dissolve in hot HCl (1·12), and treat by *P. 65*a*).

Notes.

1. With regard to the test for iron with KCNS and the necessity of removing the HNO_3, see P. 64, N. 2.

2. This method of separation depends on the facts that, upon boiling an acetic acid solution containing much acetate, ferric iron and titanium are completely precipitated, and thallic thallium and zirconium nearly so, in the form of a basic acetate or hydroxide; and that all the phosphate present combines with these elements when they are present in excess, and therefore it then passes completely into the precipitate, leaving the bivalent elements in solution. This behaviour of the phosphate is due to the fact that the solubility in acids of the phosphates of the trivalent and quadrivalent elements is much smaller than that of the phosphates of the bivalent elements.

3. If upon adding the ammonium acetate the solution becomes of a reddish colour, it shows that iron is present in quantity more than sufficient to combine with the phosphate; for a cold solution containing ferric acetate is of a deep red colour. If, on the other hand, a colourless solution results (either with or without a precipitate), it shows that there is no excess of iron, and $FeCl_3$ is therefore added, which causes the precipitation of $FePO_4$ as a yellowish white precipitate. Upon boiling, the excess of iron separates completely as a dark red gelatinous precipitate of basic ferric acetate, leaving the supernatant liquid colourless, except when nickel or cobalt is present.

4. The solution is diluted to at least 100 cc., owing to the large volume of the precipitate, and it must be heated in a capacious flask owing to its tendency to boil over.

*5. Zirconium may not be completely precipitated under the conditions of this procedure, 1 to 5 mgrms. sometimes remaining in solution, especially when considerable acetic acid is present. To ensure its complete separation, the filtrate is made alkaline with NH_4OH.

*6. The precipitation of thallium in this procedure is not quite complete, but there is no danger of losing even 0·5 of a mgrm. when iron is also present, as is always the case.

**Procedure* 65*a*.—To the HCl solution (P. 64 or 65, and *62*a*) which should be of specific gravity of 1·11—1·12, add 10 to 20 cc. more HCl (1·12), transfer the (cold) solution to a separating funnel, add an equal volume of ether, shake vigorously several times (preferably after inverting the funnel and opening the cock), and then allow the two layers to separate. Draw off the layers separately, and rinse out the funnel with a little ether. Return the aqueous layer to the funnel, and treat it with ether as before; if necessary, repeat this treatment once or twice until the ether layer remains colourless. (Water solution, *P. 65*b*; first ether solution, *P. 65*d*; remaining ether solutions, reject).

Notes.

1. If the directions are followed, 97 to 99 per cent of the $FeCl_3$ present passes into the ether layer in each extraction. It is evident from this statement, that even when 500 mgrms. of iron are present, substantially all of it will be removed in three extractions. But it is important that the concentration of the HCl solution in contact with the ether layer lie within the narrow limits of 20 to 22 per cent HCl, corresponding to a specific gravity of 1·10 to 1·11 at 15°. This concentration is realised in the procedure, even though a little stronger acid is used, for some of the HCl passes into the ether layer. The extraction of the $FeCl_3$ is less complete both with stronger and weaker HCl solutions; thus with HCl containing initially either 18 or 25 per cent about 94 per cent of the $FeCl_3$ passes into the ether layer; while with 8 per cent HCl only 4 or 5 per cent of the $FeCl_3$ was extracted in each shaking. Almost all the thallium, which is present as $TlCl_3$, also passes into the first ether extract.

2. The following are probably the principles involved in this ether extraction. Since iron passes into the ether layer only in the form of $FeCl_3$, the quantity of it extracted by the ether increases in accordance with the distribution law, the larger the proportion of un-ionised anhydrous $FeCl_3$ in the water layer. This proportion is, however, increased by increasing the concentration of HCl both in virtue of the reduction of the ionisation by the common-ion effect, and of the reduction of the hydrolysis of the ferric salt by the free acid. It is doubtless true that the strong acid has also a dehydrating effect, thereby increasing the anhydrous $FeCl_3$ in the water layer. As the HCl becomes very concentrated, however, another effect, opposite in character, comes into play; namely, ether dissolves in large quantities in the aqueous layer, and HCl and water dissolve in large quantity in the ether layer, thus making the two layers more nearly alike, and doubtless decreasing the distribution-ratio for the $FeCl_3$ between the ether and water layers. With respect to this explanation, it should be added that it is uncertain to what extent complex acids $HFeCl_4$, &c.) may be involved.

3. Since the colour of the ether layer is a sensitive indication of iron, the treatment with ether may be discontinued as soon as a nearly colourless ether extract is obtained. When titanium is present the water layer may remain distinctly yellow, owing to the presence of hydrogen peroxide as impurity in the ether; such a colour does not therefore show that iron is still present.

4. Titanium and zirconium remain completely in the water layer. When much zirconium is present some of it may be precipitated out as chloride, but this remains suspended in the water layer.

5. Phosphoric acid does not interfere with this separa-

* From the *Journal of the American Chemical Society*, xxx., No. 4.

tion, and the iron can therefore be extracted even after the basic acetate procedure.

**Procedure 65b.*—Heat the HCl solution (*P. 65*a*) on a water-bath until the ether is expelled, add 1 cc. H_2SO_4 (1·20), evaporate almost to dryness until the H_2SO_4 begins to fume, adding 1 cc. more H_2SO_4 (1·20) if the residue is solid. If the residue is dark coloured, owing to organic matter, add a few drops HNO_3 (1·42), and evaporate again until the H_2SO_4 begins to fume. Cool, add 5 cc. water, 10 cc. 3 per cent H_2O_2 solution, and then 10 cc. 10 per cent $Na_2HPO_4.12H_2O$ solution. (Orange-yellow to orange-red solution, presence of *titanium*; white flocculent precipitate, presence of *zirconium*). Let the mixture stand for at least an hour, filter, and wash the precipitate. (Filtrate, if coloured, *P. 65*c*; precipitate, Note 3).

Notes.

1. By the addition of H_2O_2 titanium is converted into a sulphate corresponding to the higher oxide TiO_3, the red colour being due to the cation. This colour test is an extremely delicate one, even 0·1 mgrm. Ti imparting a distinct yellow colour to the solution.

2. By the Na_2HPO_4, zirconium is precipitated as a basic phosphate, $Zr(OH)PO_4$. Its precipitation is slow; but, if nothing has separated after half-an-hour, it is safe to conclude that less than 0·5 zirconium is present, provided care has been taken not to use more H_2SO_4 than is directed in the procedure. If the titanium had not been oxidised by the addition of H_2O_2, it would also give an entirely similar precipitate of $Ti(OH)PO_4$; but from a solution containing H_2O_2 in excess when titanium is alone present none of it separates even on standing several hours. When zirconium and titanium are present together, a small proportion of the titanium is carried down with the zirconium, and the phosphate precipitate may then have a distinct yellow colour.

3. Some of the rare earth elements, such as thorium, may also be precipitated as phosphate at this point, if these elements have not been proved absent or removed in *P. 52*a*. In such a case the presence of zirconium may be proved by pouring a portion of dilute HF several times through the filter (supported in a celluloid funnel or a platinum ring), evaporating with H_2SO_4 in a platinum dish, diluting, and adding NH_4OH. The rare earth phosphate would be left undissolved by the HF.

4. Besides titanium and zirconium, the solution from *P. 65*a* will sometimes contain uranium, manganese, and cobalt (carried down in the precipitates in P. 52, *P. 62*a*, and P. 64, respectively), but not in sufficient amount to interfere with the zirconium and titanium tests. The only other element of the aluminium and iron groups that gives a similar colour with H_2O_2 in acid solution is vanadium; but this, aside from the fact that it should not be present, would give no precipitate with Na_2HPO_4 (not even on the addition of Na_2SO_3 in *P. 65*c*).

(To be continued).

CORRESPONDENCE.

APPOINTMENT OF PUBLIC ANALYST FOR THE METROPOLITAN BOROUGH OF SHOREDITCH.

To the Editor of the Chemical News.

Sir,—I am directed to bring to your notice the following letter which has been addressed to the Town Clerk of the Metropolitan Borough of Shoreditch,—I am, &c.,

Richard B. Pilcher,
Registrar and Secretary.

The Town Clerk, Metropolitan Borough of Shoreditch.

Dear Sir,—The attention of the Institute of Chemistry has been directed to the terms of an announcement to the effect that the Council of the Metropolitan Borough of Shoreditch is about to appoint a Public Analyst in the place of the late Sir Thomas Stevenson.

The Council of the Institute, while feeling that they need not impress on the Borough Council the great importance of securing the services of a fully competent analyst, desire me to express their regret that the appointment should have been offered in terms which might suggest that it is to be given to the candidate making the lowest tender.

My Council venture to express the opinion that, in the case of an appointment of this kind, the qualifications for which are of a purely personal character, the system of inviting professional men to tender for an appointment has the effect of lowering the status of their profession, to the detriment of the public service. It precludes, and in this case has precluded, many analysts of repute from becoming candidates for the appointment, and therefore limits the selection, while it is not likely that the Borough Council will secure the services of the best man by entrusting the position to the practitioner who places the least value on his skill, experience, and professional position.

I am desired to request you kindly to bring this letter to the notice of the Borough Council when the appointment in question is under consideration.—I beg to remain, dear Sir, yours faithfully,

(Signed) Richard B. Pilcher,
Registrar and Secretary.

A similar communication has been addressed to the Town Clerk of the City of York.

COMPULSORY WORKING OF PATENTS.

To the Editor of the Chemical News.

Sir,—Needless anxiety has been caused to hundreds of patentees by the inaccurate statements which have appeared in the public press concerning the provision contained in the Patents and Designs Act, 1907, relative to the "working" of patents in this country, and I regret that I find the same inaccuracy in Prof. Kipping's Address to the Chemical Section at the recent meeting of the British Association, as reported in your issue of 11th September.

The sole ground connected with "working" on which any person may apply for the revocation of a patent is that "the patented article or process is manufactured or carried on exclusively or mainly outside the United Kingdom."

It is only when he is satisfied that the allegation to the above effect by the person making the application is correct that the Comptroller can call upon the patentee to show that the article or process is being manufactured or carried on to an adequate extent in the United Kingdom.

It follows that patentees whose patents are not being "worked" abroad have no reason to fear for the safety of their patents on this ground.

The inaccuracy in no way affects Prof. Kipping's able review of the position of chemical industry in this country, but it is desirable that inventors should not be misled as to their position.—I am, &c.,

A. G. Bloxam.

Birkbeck Bank Chambers, W.C.,
September 14, 1908.

Oxidation of Isoeugenol. Dehydrodiisoeugenol.—H. Cousin and H. Hérissey.—The oxidation of isoeugenol with iron perchloride gives a white crystalline substance, which appears to be dehydrodiisoeugenol, isomeric with dehydrodieugenol. The same compound is formed by the oxidising action upon isoeugenol of the ferment in mushrooms. The authors have prepared the dimethyl, diacetic, and dibenzoic ethers of dehydrodiisoeugenol.—*Comptes Rendus*, cxlvii., No. 4.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvii., No. 4, July 27, 1908.

Gases Occluded in a Special Nickel Steel.—G. Belloc.—The gases occluded in a nickel steel containing 45 per cent of nickel and 0·15 per cent of carbon are carbon dioxide, carbon monoxide, hydrogen, and nitrogen. In the turnings of the steel the total volume of gas is three and a-half times the volume of the alloy. The t, dv/dt curve is practically parallel to the temperature axis; the proportion of carbon monoxide increases up to 75 per cent, while the hydrogen has a maximum at 540° and then regularly decreases. With the wire the total volume of gas is ten times that of the metal; the t, dv/dt curve has two marked maxima—one at 540° and the other at 830°; the variations in the composition are not progressive. At 540° the carbon monoxide is at a minimum and the hydrogen at a maximum. Above this temperature the carbon monoxide increases irregularly. The alloy belongs to the class called by Guillaume "reversible," and at 350—400° the beginning or end (according as the temperature is increasing or decreasing) of the progressive transformation occurs. The extraction of most of the gases is effected when the iron is in the γ-state and the nickel in the β-state, and a regular increase in the proportion and composition of the gases such as occurs with the turnings is to be expected. The difference between the absolute volume of the gas extracted from the wire and the turnings may be explained by one of the following hypotheses:—(1) A very heterogeneous distribution of the gases in the alloy; (2) a loss of occluded gas due to the mechanical action of the drill; (3) an absorption of gas during the operation of drawing into wire.

New Method of Determining the Fixed and Volatile Acids in Wines.—Emm. Pozzi-Escot.—100 cc. of the wine are evaporated to 3 to 4 cc., treated with excess of alcohol, and filtered. The filter is ignited in a muffle furnace, and thus the insoluble salts of the wine are determined. Their alkalinity is determined by titration with nitric acid. Another 100 cc. of the wine are evaporated to 3 to 4 cc., neutralised with baryta, and 100 cc. of alcohol at 96°, containing 2 per cent of barium bromide, are added. The fixed acids are thus precipitated as barium salts, and the volatile acids remain in solution. The precipitate is filtered off, ignited, and titrated with nitric acid. The difference between the first titration and the second gives the fixed acids, A_f. The fixed acids minus the total acidity of the wine, A_t, gives the volatile acids, A_v. Thus, $A_f - A_t = A_v$. This method does not give exact results in presence of lactic acid, which, however, is exceptional in wines, and, moreover, it can only be used for organic acidity.

New Method of Preparing Mixed Anhydrides of Organic Acids.—J. Bougault.—When phenylisocrotonic acid is treated with iodine in presence of a very large excess of sodium carbonate, benzoylacrylic acid, $C_6H_5—CO—CH=CH—CO_2H$, is formed. If a sufficient quantity of the sodium salt of an aromatic acid is added to the aqueous solution containing sodium phenylisocrotonate and carbonate in excess, and then iodine is added gradually, the mixed anhydride of benzoylacrylic acid and the aromatic acid employed is obtained. By this method the author has prepared various mixed anhydrides, *e.g.*, benzoic-benzoylacrylic, $C_6H_5—CO—CH=CH—CO\rangle O$, $C_6H_5—CO\rangle$, and has investigated their properties.

Constitution of Vicianine.—Gabriel Bertrand and G. Weisweiller.—Vicianine (a glucoside found in the seeds of *Vicia augustifolia*) resembles amygdaline, but is distinguished from it by its physical constants. It contains a CH_2O group more than amygdaline. With concentrated sulphuric acid in the cold a carmine red coloration s produced which is characteristic of the group $C_6H_5—CH\langle^{CN}_{O}$. The presence of this group is confirmed by two reactions:—(1) The liberation by hydrolysis with diastase of one molecule of benzoic aldehyde and one molecule of hydrocyanic acid. (2) The production of phenylglycolic acid by the hydrating action of mineral reagents. Thus vicianine, like amygdaline, is a derivative of lævophenylglycolic nitrile.

MISCELLANEOUS.

East London College.—The Drapers' Company have voted special grants for the purchase of important additions to the equipment of the Engineering Department, the staff and students of which have carried out a series of tests of vanadium and other special steels which are being largely used in the construction of high-speed engines. The recent installation in the Electrical Engineering Department of an 11 kilowatt rotatory converter of special design should be of great use to senior students, and to those seeking to carry out standardisation experiments. The list of academic distinctions gained by students of the College affords proof of the many-sided activity of a modern University College. In the Faculty of Arts, two students obtained the degree of Master of Arts in mathematics. In the Faculty of Science, one student is made Doctor of Science, and another Bachelor of Science for research in branches of Chemistry, a subject which is particularly well developed at the College. So far as the Internal Honours Examinations of London University are concerned the College does well in Science (three first classes), and almost as well in Engineering, where two first classes are won, although the Faculty of Engineering is here, as elsewhere, in point of numbers much smaller than either the Faculty of Arts or of Science. Mr. W. Lower Carter, M.A., has been apppointed Lecturer in Geology.

Birkbeck College.—The 86th Session of the College will commence on Monday, September 28th. An Opening Address will be given in the theatre, at 7.30 p.m., by Dr. Albert Griffiths. The College will be open for inspection after the Address. Visitors are invited. The College is conducted in close relation with the University of London; twenty-eight Members of the Staff are Recognised Teachers of the University; and the courses of study provide for Degrees in the faculties of Arts, Science, Laws, and Economics. The Laboratories are well-equipped with modern apparatus and appliances, and Research Work is encouraged in the various Science Departments (Chemistry, Physics, Botany, Zoology, and Geology). According to the Calendar more than one hundred Students passed some Examination of the University during the last Session; several Students gained Scholarships at the older Universities; one obtained the London University Scholarship in English, and one obtained a City Parochial Foundation Scholarship. Eleven Students gained Assistant Examinerships in the Patent Office, twelve gained appointments as Assistant Surveyors of Taxes, and other public appointments were obtained. The Arts Subjects include Courses in English, Classics, French, German, Italian, History, Logic, Mathematics, Economics, and Geography, all conducted by Recognised Teachers of the University. The Law Courses comprise Mercantile and Common Law, Equity, Conveyancing, and Patent Law, and Classes in English and Roman Law, and Constitutional Law and History. There is also an Art School, which provides instruction in the various Branches of Artistic Work (Painting, Modelling, Life, &c.). Classes are held both in the Day and in the Evening.

NOTES AND QUERIES.

Dyes Soluble in Petrol.—We are anxious to get all the information we can on dyes soluble in petrol or benzine. All aniline and other dyes which we have been able to test do not appear to be soluble in petrol, and we are anxious to know whether there are any dyes made, preferably red and blue, which would suit our purpose. If you can kindly give us any information on this subject, or refer us to any books or papers, we should be very grateful.—C. C. WHARTON.

THE CHEMICAL NEWS.

Vol. XCVIII., No. 2549.

A DEMONSTRATION IN THE RAPID ELECTRO-ANALYTICAL SEPARATION OF METALS.*

By HENRY J. S. SAND.

In the process of electro-analysis to be shown the principle of very vigorous stirring of the electrolyte has been combined with that of keeping the potential of the cathode under control by means of an auxiliary electrode. It has thus been possible very largely to extend the scope of electro-analytical methods. The following metals have hitherto been studied :—First, the metals of the silver and copper groups and zinc, *i.e.*, silver, mercury, copper, bismuth, lead, cadmium, and zinc. These metals have all been deposited singly, separated from each other, and also separated when all present in the same solution. In the last-named case the quantity of each metal taken varied between 0·10 and 0·15 grm., and the time for the deposition of each between about ten and fifteen minutes (*Trans. Chem. Soc.*, 1907, xci., 373). Secondly, new methods have been elaborated for the determination and separation from each other of antimony and tin. A considerable number of determinations have been carried out in which the metals taken in varying ratios weighed together approximately 1 grm. The time for the deposition of the antimony was usually about twenty minutes, that for the tin about eighty minutes. Lastly, the possibility has been examined of securing a purely electro-analytical method for the analysis of an alloy consisting of copper, antimony, lead, and tin, and all the separations required for such an analysis have at the present time been carried out.

THE PRODUCTION OF AMMONIA FROM ATMOSPHERIC NITROGEN BY MEANS OF PEAT.*

By H. C. WOLTERECK, Ph.D.

Attempts to utilise the nitrogen contents of peat have been made during the last sixty years, but the yield of ammonia obtained by the various processes which have been tried shows that only about one-third of the nitrogen can be thus recovered. Starting from an observation that a mixture of nitrogen and hydrogen passed over reduced iron at a low heat always produced ammonia for some time, the author made further experiments on these lines, and found that the presence of oxygen and water was of importance. This led to the gradual reduction of the quantity of hydrogen, and finally to its complete omission; but the periodical necessity of reducing the iron used for the purposes of moist oxidation led him to employ some carbonaceous material (coke, coal, charcoal, &c.), for this purpose.

Finally, peat was found to give the most satisfactory and rapid results, and even when it contained up to 80 per cent of water it could be utilised advantageously.

In the meantime experiments were made to prove the co-operation of atmospheric nitrogen. Sugar carbon absolutely free from nitrogen was treated by the process, and produced an average of 1 per cent ammonia on the carbon consumed.

The large plant erected at Carnlough, Co. Antrim, has finally confirmed the working and results of the process on a commercial scale.

* A Paper read before the British Association (Section B), Dublin Meeting, 1908.

THE INFLUENCE OF COLLOIDS AND COLLOID SUSPENSIONS ON THE SOLUBILITY OF CARBON DIOXIDE IN WATER.*

(Preliminary Note).

By ALEX. FINDLAY.

The problem of the absorption of gases, more especially oxygen and carbon dioxide, by blood is one which has exercised the minds of physiologists and physicists for many years, the view generally held being that the gases are retained in the blood largely owing to the formation of chemical compounds. With regard to the absorption of CO_2, the reputed alkalinity of the blood, and the consequent formation of carbonate and bicarbonate, have been held chiefly responsible for the increase in solubility of CO_2 in blood as compared with that in a corresponding salt solution. Recently, however, various investigators (Holber, Farkas, Fraenkel, &c.) have shown that blood is "water neutral," in which case the generally held view regarding the absorbtion of CO_2 by blood becomes untenable.

Believing that the colloids present in blood might very probably play an importan *rôle*, it was decided to undertake an extended investigation of the influence of colloids on the absorption of gases by water, since only a very few experiments in this direction have been carried out (Geffchen).

The following results have been obtained by Mr. W. H. Harby, B.Sc., working under the direction of the author. All determinations were made at 25°, and the solubility values represent the ratio of gas volume absorbed to the volume of the absorbing liquid :—

I. Solubility in water, 0·823. Experimental error about ± 0·25 per cent.				
II. Colloidal ferric hydroxide—				
Grms. of $Fe(OH)_3$ in 100 cc. of liquid	1·36	0·68	0·34	0·136
Solubility of CO_2 .	0·896	0·877	0·837	0·824
III. Gelatin—				
Grms. of gelatin in 100 cc. of liquid .	5	3	1	
Solubility of CO_2 .	0·848	0·834	0·826	
IV. Arsenious sulphide—				
Grms. As_2S_3 in 100 cc. of liquid .	0·305	0·244	0·122	0·0244
Solubility of CO_2 .	0·822	0·825	0·825	0·825
V. Silicic acid—				
Grms. H_2SiO_3 in 100 cc. of liquid .	0·113		0·068	
Solubility of CO_2 .	0·823		0·822	
VI. Dextrin—				
Grms. of dextrin in 100 cc. of liquid .	20	10	5	1
Solubility of CO_2 .	0·735	0·757	0·768	0·817
VII. Soluble starch—				
Grms. of starch in 100 cc. of liquid .	10	5	1	
Solubility of CO_2 .	0·776	0·801	0·815	
VIII. Glycogen—				
Grms. of glycogen in 100 cc. of liquid	1·18		0·263	
Solubility of CO_2 .	0·804		0·820	
IX. Albumen—				
Grms. of albumen in 100 cc. of liquid	0·5		0·75	
Solubility of CO_2 .	0·822		0·822	

Experiments, still in progress, have been made with the white of egg, diluted with five times its volume of water. An increase of about 8 per cent in the solubility of CO_2 was found. Soon, however, a precipitate began to form, and the solubility of CO_2 diminished, some of the gas which had been dissolved passing out of solution. Finally, there was an increase in the solubility of about 4 per cent.

* A Paper read before the British Association (Section B), Dublin Meeting, 1908.

THE TRANSFORMATION OF AROMATIC NITROAMINES AND ALLIED SUBSTANCES, AND ITS RELATION TO SUBSTITUTION IN BENZENE DERIVATIVES.*

I. *Transformation of Nitroaminobenzenes into Nitroanilines.*

(With W. W. REED, M.Sc., A.I.C.

THE investigation of the transformation of 2·4-dichloro-1-nitroaminobenzene into 2 : 4-dichloro-6-nitroaniline, reported on last year (*Brit. Assoc. Reports*, 1907, p. 101) has been continued.

Transformation of the Crystalline Nitroamine.

The object of the new experiments on the transformation of the crystalline nitroamine was to determine with greater accuracy the limiting value of the pressure of the gaseous catalyst, below which no transformation occurred. The method employed was substantially that described in last year's Report, but more elaborate methods were used for determining the partial pressure of the reagent, hydrogen chloride. The form of the experimental tube was so modified that, after the change had occurred (or failed to occur), the tube could be opened, attached to a Sprengel pump, and its exact volume measured by collecting the air, filling it at a given temperature and pressure. The hydrogen chloride was introduced as dilute standardised solutions, known weights of which were used. A series of such experiments has shown that at 13° the hydrogen chloride must be at a pressure of 14 mm. of mercury for a change to take place.

Transformation of the Nitroamine in Solution.

Inasmuch as the nitroamine is colourless, whilst the nitroaniline is intensely coloured, the change can be quantitatively followed by comparing the colour of the solution, during the course of the transformation, with that of standard solutions of the nitroaniline. The method is exceedingly delicate ; with practice it is easy to detect the difference in tint between 49 and 50 cc. of a solution of nitroaniline containing 0·000225 grm. in 100 cc. when the tint of these volumes is compared in columns 12 cm. in length ; that is 0·00225 mgrm. of the aniline can be measured.

The low solubility of the nitroaniline (100 cc. at 14° dissolve 0·0022 grm.) allows only of the use of solutions of the nitroamine containing 0·003 grm. per 100 cc. in these experiments.

The measurements of the speed of transformation show that the reaction is one of the first order. The change into the nitroaniline is accompanied by a conversion (reduction) of the nitroamine into diazonium salt to the extent of 30 per cent. This fact only permits of the determination of an apparent value of the velocity coefficient.

Solvent.—The only solvents which could be used were water, acetic acid, or mixtures of these. Alcohol and acetone, which are solvents of the catalysts, react with the nitroamine.

As the proportion of the acetic acid in the solvent is increased the rate of change slowly rises until, with 74 per cent acetic acid, the rate is double that in pure water. But the use of higher concentrations of acetic acid is followed by a rapid rise in the speed of the change, which in glacial acetic acid is several hundred times as great as in water.

ii. *Nature of the Acid (Catalyst).*—The efficacy of acids as catalysts in this transformation is roughly in the order of their activities as measured by other reactions. Nevertheless, chloric and perchloric acids appear to bring about the change twice as rapidly as hydrochloric acid, although they are somewhat less active as catalytic accelerators in hydrolyses, &c. The reduction of the nitroamine to diazo-compound is, however, much less in the case of these acids, a fact which may account for the more rapid formation of nitroaniline.

Hydrobromic and hydriodic acids reduce the nitroamine ; the former reacts quantitatively according to the equation $Ar.NH.NO_2+3HBr=Ar.N_2Br_3+2H_2O$, the diazonium perbromide crystallising out when acetic acid is the solvent. Hydriodic acid carries the reduction further.

iii. *Concentration of the Acid.*—The effect of the concentration of the acid catalyst on the rate of change has been carefully tested with several acids both in aqueous and acetic acid solution.

In aqueous solution the rate is proportional to the square of the concentration of the acid—that is, on doubling the concentration of the acid the velocity is quadrupled.

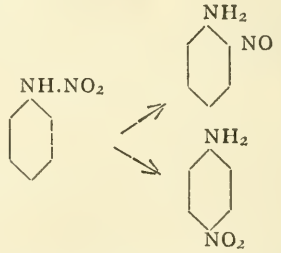
In acetic acid solution this proportionality does not hold, the increase of velocity being less for given increases of concentration of acid. For example, the ratio of the velocity coefficients for N/10 and N/20 H_2SO_4 in glacial acetic acid at 25° is $k_{N/10} : k_{N/20} = 2·14$ instead of 4.

iv. *Effect of Temperature.*—Withing a range of temperature of 0—35° the products of the transformation of the nitroamine were not modified. When the nitroamine was melted under water or other solvents, a more profound decomposition was observed accompanied by oxidation of the benzene nucleus.

In aqueous solution the rate of the transformation was greatly increased by a rise of temperature. At 25° the rate of change is approximately thirty times as great as at 0° ; the ratio of the velocity coefficients, when 2N HCl is the catalyst, at 25° and 35° C. is $k_{35°} : k_{25°} = 0·002488/0·00108 = 2·3$.

Experiments on Nitroaminobenzene, $C_6H_5.NH.NO_2$.

A number of preliminary experiments have been made with the unsubstituted nitroaminobenzene. In its main features the molecular re-arrangement of this nitroamine resembles that of its dichloro-derivative, but it is complicated by the simultaneous formation of both *o*- and *p*-nitroaniline—



Experiment has shown that the latter is only formed to the extent of some 10 per cent, but the difference in the intensity of the colours of the solutions of the nitroanilines has so far made any accurate measurement of the rate of change impossible by the method above described. Under like conditions (temperature and concentration of catalyst) the velocity is about one and a-half times greater in the case of the unsubstituted than with the dichloro-compound ; in glacial acetic acid, however, the change was roughly ten times as rapid.

Reduction to the diazo-compound also takes place, and since in this case the diazo-compound is unstable, the subsequent decomposition introduces another factor, which prevents quantitative measurements of the velocity.

The views expressed in last year's report are confirmed by these more extended observations. The most simple interpretation of the facts seem to be that the catalyst (the acid) and the nitroamine form an additive compound, which alone is capable of molecular re-arrangement.

For what reason the speed of the transformation should be proportional to the second power of the concentration

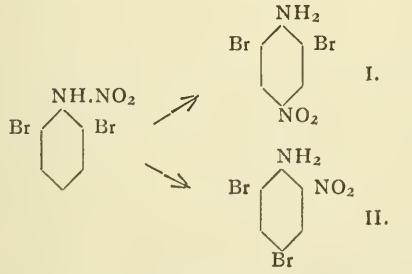
* Report of the Committee, consisting of Professor F. S. Kipping (Chairman), Professor K. J. P. Orton (Secretary), Dr. S. Ruhemann, Dr. A. Lapworth, and Dr. J. T. Hewitt. Read before the British Association (Section B), Dublin Meeting, 1908.

of the acid is not very obvious. Blanksma (*Recueil des Trav. Chim.*, 1903, xxii., 290) observed that the rate of the analogous transformation of acetylchloroaminobenzene into *p*-chloroacetanilide bore the same relation to the concentration of the hydrogen chloride, which is the only catalytic accelerator of this change. Acree (*Am. Chem. Journ.*, 1907, xxxviii., 258) has suggested that the existence of the additive compound of the chloroamine and the catalyst is conditioned by the equilibrium, $Ar.NClAc,HCl \rightleftarrows Ar.NCl.Ac + H^{\circ} + Cl'$, when the concentration of the complex would depend on the square of the concentration of the acid. That the ratios of the accelerating effects of hydrochloric, nitric, and sulphuric acids, $k_{Hce} : k_{HNO_3} : k_{H_2SO_4} = l : l : 2/3$, are approximately in their ratio of their ionisation in normal solutions is in harmony with this view.

II. *The Wandering of Bromine in the Transformation of Nitroaminobromobenzenes.*

(With C. PEARSON, B.Sc.).

In the transformation of 2 : 6-dibromo-1-nitroaminobenzene, in all circumstances when such a change will take place, we have observed a remarkable re-arrangement of the points of attachment of the substituting groups.



Not only is the normal product, 2 : 6-dibromo-4-nitroaniline I., in which the nitro group passes to the vacant para-position formed, but also 2 : 4-dibromo-6-nitroaniline II. In the production of the latter compound, the migrating nitro group displaces one ortho-placed bromine atom, which then becomes attached to the para-carbon atom.

The direct nitration of 2 : 6-dibromoacetanilide is not accompanied by any such re-arrangement; the nitro group only enters the para-position.

NOTE ON A VOLATILE COMPOUND OF COBALT WITH CARBON MONOXIDE.*

By Dr. LUDWIG MOND, Dr. HEINRICH HIRTZ, and M. DALTON COWAP.

IN a previous paper (*Journ. Chem. Soc.*, 1890, p. 749), published by one of us in conjunction with Dr. Carl Langer and Dr. F. Quincke, entitled "Action of Carbon Monoxide on Nickel," p. 752, we stated that "numerous experiments made to obtain similar compounds of carbon monoxide with other metals, notably with cobalt, iron, copper, and platinum, have only led to negative results." In a later paper (*Journ. Chem. Soc.*, 1891, p. 604), published by one of us in conjunction with Dr. F. Quincke, we announced the formation of iron carbonyls, which were subsequently more fully described by one of us in conjunction with Dr. Carl Langer (*Journ. Chem. Soc.*, 1891, p. 1091).

In continuing the experiments with cobalt and taking advantage of the method of Sir James Dewar for facilitating the formation of nickel carbonyl by acting upon the finely divided metals by carbon monoxide under a high pressure and correspondingly high temperature instead of working at ordinary pressure and ordinary temperature as we had hitherto done, we succeeded in obtaining small quantities of a cobalt carbonyl when the pressure was raised to 50 atmospheres and the temperature to 150° C., and the quantity formed was considerably increased by raising the pressure to 100 atmospheres and the temperature to 200° C.

The cobalt oxide was prepared from a pure oxalate, free from nickel and iron, by heating to about 200° C. The sketch exhibited gives the apparatus in which we have obtained the cobalt carbonyl. The cobalt oxide was filled into a steel retort, which was fitted with two steel pipes for the gas circulation. All iron parts were lined with copper so as to prevent the action of carbon monoxide on the iron. This retort was heated in an oil-bath. Behind the outlet valve we fixed a small gun-metal cylinder, which contained a filter of flock asbestos, and behind this we had an additional filter of cotton-wool in a glass tube. From there the gases had to pass a condensing bottle, and the spent gases were burnt at outlet. The cobalt oxide was placed into the retort and reduced with hydrogen at 5—10 atmospheres pressure, and at the lowest possible temperature. A slow current of carbon monoxide was then passed through the apparatus at 100 atmospheres pressure. The temperature of reaction lies between 150° C. and 200° C. Both filters were kept at 50° C. by means of warm water. The condensing bottle was cooled in ice. In this bottle we obtained large orange crystals of the cobalt carbonyl.

The analysis of these crystals was made by decomposing them with bromine water. The carbon monoxide was measured and the cobalt estimated in the solution. The result was :—

Co.	CO.	Co : CO.
0·0744 grm.	0·1597 grm.	1 : 3·96
0·0582 „	0·1115 „	1 : 4·03

We conclude, therefore, that this compound is $Co(CO)_4$, corresponding to the liquid nickel carbonyl.

The cobalt carbonyl is gradually decomposed in air, leaving a deep violet substance, which has not yet been investigated. The crystals are best preserved by sealing them in a glass tube under hydrogen or carbon monoxide. The cobalt carbonyl is very slowly attacked by non-oxidising acids, as hydrochloric or sulphuric. The reaction is accelerated by the presence of an oxidising agent. The carbonyl is quickly, almost instantaneously, decomposed by oxidising acids, such as bromine, chlorine, nitric acid, and the corresponding cobalt salt is formed under elimination of carbon monoxide, according to the following equation—$Co(CO)_4 + Br_2 = CoBr_2 + 4CO$. The cobalt carbonyl is insoluble in water, but more or less soluble in the several organic solvents, such as carbon bisulphide, ether, naphtha, alcohol, and nickel carbonyl. If these solutions are kept standing for some time, or if they are warmed, decomposition sets in. These and other solutions and their products of decomposition have not yet been investigated.

The specific gravity measured by the suspension method at 18° C. is 1·827, but we do not yet regard this figure as final, as the substance is so easily decomposed, and if only kept for a few hours the specific gravity increases considerably, due to decomposition. The vapour tension *in vacuo* could not be measured with certainty owing to decomposition. The vapour tension at 15° C. measured 11 mm., but already at 25° C., decomposition could be proved, which was already very marked at 35° C., so that we are not sure if there was not already a slight decomposition at 15° C. In a carbonic oxide atmosphere the decomposition commences at about 40° C. to 45° C., and is complete at 130° C. to 135° C., leaving metallic cobalt.

The melting-point lies between 42° C. and 46° C. We could not estimate it more exactly owing to its decomposition.

* A Paper read before the British Association (Section B), Dublin Meeting, 1908.

The authors reserve for themselves the right to further examine this reaction with other metals.

The Laboratory,
20, Avenue Road, Regent's Park, London, N.W.,
June 22, 1908.

SOME REACTIONS OF DICHLORO UREA.*

By F. D. CHATTAWAY, D.Sc., F.R.S.

UREA is so well known and has been so much investigated that any new simple substance obtainable from it posesses quite an unusual amount of interest. Such a new substance is found in dichloro urea, which, leaving out of consideration the derivatives of ammonia itself, is one of the simplest possible compounds containing halogen attached to nitrogen. It is produced when chlorine is passed into a cooled saturated aqueous solution of urea. Action takes place without any considerable development of heat, and dichloro urea crystallises out as a white powder consisting of small transparent plates. It can be preserved for a considerable time in a dry atmosphere, although it is not a very stable body. It is comparatively safe to handle, and promises to be of considerable use as a synthetic agent, as it is easily soluble in water, alcohol, and ether, and is very reactive. Its composition shows that it has the formula $CON_2H_2Cl_2$, and having regard to its mode of formation as well as to the structure of urea itself, its constitution is most probably represented by the formula $OC<^{NHCl}_{NHCl}$.

By means of this formula its formation and such of its reactions as have yet been studied can be explained. The other theoretically possible chloro substitution derivatives of urea, though probably formed in the reaction between chlorine and urea, have not so far been isolated.

When dichloro urea is produced, although two molecules of hydrogen chloride are formed, very little heat is developed, and it must therefore be an endothermic compound, and might be expected to be highly explosive. When heated, however, it does not itself explode, but decomposes at about 83°, with liberation of nitrogen chloride, which latter may detonate with great violence if not allowed to escape, and if the temperature is raised a few degrees higher, as, for example, when dichloro urea is heated in a test-tube over a water-bath.

Dichloro urea gives all the characteristic reactions of a typical nitrogen chloride; for instance, it liberates iodine from hydriodic acid, chlorine from hydrochloric acid, and reacts with alcohol, forming ethyl hypochlorite, urea being in each case re-formed.

Dichloro urea is distinguished from most other substituted nitrogen chlorides by the readiness with which it is hydrolysed, nitrogen chloride, carbon dioxide, a little nitrogen, and ammonium chloride being formed. If the compound is dissolved in water or kept in a moist atmosphere, this hydrolysis takes place slowly at the ordinary temperature, and becomes very rapid at about 30° C.

It is probable that in this reaction a mono-substituted ammonia is first produced thus—

$$CO<^{NHCl}_{NHCl}+2H_2O=CO<^{OH}_{OH}+2NH_2Cl.$$

But if so, it apparently can only exist momentarily, as nitrogen chloride is at once liberated. The formation of the end products of the reaction can be explained by assuming that this monochloro ammonia immediately breaks up into ammonia and nitrogen chloride. $3NH_2Cl=2NH_3+NCl_3$, which then to some extent react in the ordinary way, forming nitrogen and hydrogen chloride, the latter at once combining with the free ammonia, and allowing the remaining nitrogen chloride to escape, as this does not react with ammonium chloride.

Both acids and alkalis accelerate the rate of hydrolysis, and further alter the nature of the end products by hindering or furthering the secondary reaction between the ammonia and the nitrogen chloride. In presence of dilute acids the ammonia is at once fixed, and the reaction between it and the nitrogen chloride, with its accompanying liberation of nitrogen, is prevented; all the chlorine contained in the dichloro urea is therefore liberated as nitrogen chloride. In presence of alkalis, on the other hand, the reaction between the ammonia and the nitrogen chloride goes on to completion since the hydrochloric acid formed in it is at once fixed; no nitrogen chloride therefore is set free since twice as much ammonia as is required to decompose it is present.

The reaction between dichloro urea and a solution of caustic potash is very energetic; nitrogen is liberated with effervescence, the excess of ammonia and the alkaline carbonate formed remaining dissolved in the liquid. The action, which is quantitative, is expressed by the equation—

$$3CO<^{NHCl}_{NHCl}+12KOH=$$
$$=3K_2CO_3+2NH_3+6KCl+2N_2+6H_2O.$$

This behaviour of dichloro urea with alkalis affords an insight into what occurs when urea is decomposed either by an excess of alkaline hypochlorite or hypobromite. The course of this reaction has never hitherto been explained, although it has received an unusual amount of attention on account of its furnishing a ready method of estimating the quantity of urea present in a liquid. In this reaction the urea is without doubt converted into a chloro or bromo urea, which is at once hydrolysed in the manner above described. It is possible that in presence of excess of hypochlorite or hypobromite a tri- or tetra-substitution product may be produced, the formation and decomposition of which can be formulated easily, but this does not affect the essential character of the reaction, which is one of halogen substitution followed by hydrolysis of the substituted urea and interaction between ihe resulting compounds.

A reaction which indicates the use to which dichloro urea may be put in the synthesis of simple carbon and nitrogen rings is that between it and ammonia.

When ammonia in excess is added to an aqueous solution of dichloro urea, hydrolysis, accompanied by liberation of nitrogen and formation of carbonate, occurs, but in addition diurea, $CO<^{NH.NH}_{NH.NH}>CO$, is produced, and separates in considerable quantity as a sparingly soluble crystalline powder. This is the first direct synthesis of diurea from urea itself, the compound having been previously obtained from ethyl carbonate and hydrazine.

This adds another to the very few reactions known by which nitrogen atoms can be made to link up together, and further affords an exceedingly simple synthesis of hydrazine.

Diurea, when heated with excess of strong sulphuric acid to a little above 100° C., is easily hydrolysed, carbon dioxide escapes, and hydrazine sulphate is produced. This crystallises out perfectly pure in almost theoretical amount on cooling and adding a little water.

Dichloro urea can be prepared from urea and converted into diurea so easily, and the latter can be hydrolysed so quickly, that the reactions afford a synthesis of hydrazine more adapted to prepare a small quantity than any yet described. The operations involved are so simple and can be carried out so quickly, that they are also excellently suited for showing the synthesis of a hydrazine as a lecture experiment.

* A Paper read before the British Association (Section B), Dublin Meeting, 1908.

Action of Arsenic Trichloride on Nickel and on Arseno-nickels. — Em. Vigouroux. — The action of arsenic trichloride on nickel or its arsenides between 400° and 600° gives the compound NiAs, coloured red as when it is found in nature, while at higher temperatures the shining white compound Ni_3As_2 is formed. When these substances are heated in a current of hydrogen in presence of arsenic they are transformed into a greyish powder of formula $NiAs_2$.—*Comptes Rendus*, cxlvii., No. 8.

COLLOIDAL CHEMISTRY.*

By H. R. PROCTER, M.Sc.

(Continued from p. 130).

The phenomenon of electric cataphoresis was first studied with fine mechanical suspensions, and has been employed technically for clearing turbid liquids, and more recently for drying pasty mixtures, such as alizarine paste and ground peat; currents of high potential being used. It is, however, very marked in colloid sols, and closely simulates actual electrolysis. Spring (*Bull. Acad. Roy. Belg.*, 1898, [3], xxxv., 780) and Lottermoser ("Anorganische Kolloide," p. 76), and others give the following lists as to the behaviour of particles in aqueous sols:—

Wander to Cathode (+).	*Wander to Anode* (−).
Metallic hydro-oxides generally.	Colloidal metals.
Methyl violet.	Metallic sulphides.
Methylene blue.	Silver halides.
Magdala red.	Sulphur.
Titanic acid.	Selenium.
Silica in alkaline solution.	Aniline blue.
	Indigo.
	Eosin.
	Fuchsin.
	Mastic.

Many organic colloids, and some mineral ones (*e.g.*, silicic acid), wander to the anode in alkaline and the cathode in acid solution, while certain neutral substances in water, and many others in suitable mixtures of water and alcohol, are electrically indifferent. Definite charge in relation to the medium is not therefore an essential to the colloid state, though it appears to be so to electrolytic flocculation.

From what has just been said, it may be concluded that colloidal solutions must possess a sort of pseudo-electrolytic conductivity, but if this if the case, the amount is so slight that it is difficult to decide whether it depends on the colloid particles or on the residual traces of electrolyte, from which it is impossible to free the sols, as it but slightly exceeds that of the purest attainable water. Undoubtedly the particles do carry charges; but the charges are small, and the motion slow, and the number of moving particles very small compared to the ions in an ordinary electrolyte. It is also uncertain whether the particles are actually discharged at the electrodes, though occasionally particles appear to be repelled from both poles, and to collect in the middle of the liquid, which may be due to particles which have reached the electrode and received a contrary charge, wandering backwards and encountering and attracting originally charged particles proceeding in the opposite direction.

All inorganic sols are flocculated and precipitated by the addition of electrolytes, though they vary in sensitiveness. Organic sols are much less sensitive in this respect, but are frequently flocculated by the addition of organic solvents such as ether or alcohol, to which inorganic sols are usually indifferent. The precipitate is usually termed the "gel," but the term must not be confounded with "jelly" to which many of the gels are but distantly related. Gels may be "reversible," and may readily return to the sol state on restoring the original conditions, such as removing the added electrolytes; but frequently they are "irreversible," that is, the sols cannot be restored without going through the often complicated operations by which they were originally produced.

While the phenomenon of flocculation is apparently similar in inorganic and organic sols, it probably often differs rather widely in its causes, that of inorganic sols being closely connected with the electric charges of the particles; while in organic sols, osmotic effects which will be best discussed in connection with the properties of jellies, have probably a preponderating influence. Organic sols which have received definite charges usually behave with electrolytes like the inorganic.

Spring has pointed out that "coagulation" (flocculation and precipitation) takes place in two stages, though both may proceed simultaneously. In the first, the particles flocculate or adhere in larger aggregates; and in the second, these precipitate or settle under the influence of gravity. The rapidity of this second stage is much influenced by the size and density of the aggregates and the viscosity of the liquid, while the first stage is more clearly marked by the beginning of turbidity or opalescence, and, though not usually instantaneous, is better suited to observation.

Numerous experiments have shown that in order to produce flocculation, the concentration of the electrolyte must reach a certain minimum value ("Schwellenwert"), which varies with the electrolyte and the sol from a mere trace to a considerable amount.

Below this value, lapse of time produces no change, but, once it is passed, the sol is rapidly or slowly precipitated. In each case that ion of the electrolyte which has the opposite charge to the particles of the sol, has the determining effect, which increases rapidly with its valency. It has been stated that with divalent and trivalent ions it is proportional to the square and cube of that of monovalent, and Whetham (*Phil. Mag.*, [5], xlviii., 474) has shown that such a relation can be accounted for on the theory of probabilities with certain assumptions as to the electric charge required for coagulation; but the agreement of the observed numbers with each other, and with those required by theory, is not sufficiently close to make such speculation of much importance. It is also evident that the proportion will vary with the numerical value assumed for the monovalent ion. Perhaps more important is the observation of Hardy (*Proc. Roy. Soc.*, 1899, lxvi., 110) that the specific conductivities (ionic dissociation) of acid solutions exerting equivalent coagulating powers on negative and of alkaline on positive colloids are approximate constants; while acid solutions on positive and alkaline solutions on negative colloids have very varied values. This probably simply means that free H and free OH ions each have constant precipitating values for the colloids of opposite sign, while the acid and basic ions act according to their nature and valency.

It has been stated by Spring (*Rec. Trav. Chim. Pays-Bas.*, 1900, xix., 204) and others that the superior influence of polyvalent ions was not due directly to their valency, but to the usually greater hydrolytic dissociation of their salts, and, though this has been contradicted, it is not probable that the different ionic concentration produced by hydrolysis is without influence. Jordis considers that the colloid state and its phenomena are due to complex chemical compounds (*Zeit. f. Elektr.*, 1904, x., 509; *Sitzungsber d. Phys.-med. Soc. Erlangen*, 1904, xxxvi., 47; *Zeit. f. Elektrotech.*, 1904, x., 509; and Kanter, *Zeit., Anorg. Chim.*, 1903, xxxv., 16).

When a colloid sol is precipitated by an electrolyte the resultant gel always contains a small and apparently definite quantity of the precipitating ion of opposite sign to the particles, which cannot be removed by washing without restoring the gel to the sol condition or destroying its colloidal character. This quantity is proportional to the equivalent weight of the precipitating ion, and may, in many cases, be substituted by another ion of the same sign by washing with the appropriate salt (Sinder and Picton, *Journ. Chem. Soc.*, 1895, lxvii., 63). In each case an equivalent quantity of the non-precipitating ion is set free, and in the case of the stronger acids and bases may be estimated in the residual liquid by titration. These phenomena are not confined to inorganic colloids, but are very marked in many organic colloid precipitations, and apparently the same laws hold good in many pseudo-solutions, such as that of clay or of gum-mastic in water, which are generally distinguished as mere mechanical suspensions. The phenomenon of the retention of a

* A Paper read before the British Association (Section B), Dublin Meeting, 1908.

portion of the precipitating ion with the precipitate is well known in many ionic reactions, and is usually termed "co-precipitation" or "adsorption." It is, in fact, common to all bodies of largely extended surfaces, and to jellies, though the question whether in the last case the action is surface, or extends throughout the substance, must be discussed later. Even with solids, this is still, to a certain extent, an open question. Davis (*Trans. Chem. Soc.*, 1907, xci., 1666) has shown that in the absorption of iodine by carbon, an equilibrium is established with the surface action in a few hours, but that a further absorption goes on for weeks or months, which he considers due to a solid solution. The quantity of absorbed or adsorbed substance varies with the concentration of the solution with which it is in equilibrium, relatively more being taken from weak than from stronger solutions. The laws by which it is governed show close relations to those of solution-equilibria, and the phenomenon might perhaps be not improbably described as surface-solution. If a body be brought in contact with two immiscible solvents, it distributes itself between them in a ratio which, so long as its molecular condition is the same in both solvents, is, in accordance with Henry's law, a constant fraction dependent on its relative solution-pressure in the two solvents; or if C_a and C_b be its concentration in the solvents a and b and β a constant, $C_a = \beta C_b$. If, however, its molecular weight in the solvent b is n times as great as in a, the equation takes the form $C_a = \beta C_b^{\frac{1}{n}}$. Written in a general form, where x is the weight of the absorbed substance and m that of the absorbent, while C_b is the concentration of the solution, the equation becomes $\frac{x}{m} = C_a = \beta C_b^{\frac{1}{p}}$ (see Note), where β and p are constants to be determined experimentally, and represents very appoximately most adsorption-equilibria; but it is evident that p cannot represent the molecular weight in the ordinary sense since it is seldom a whole number, and usually indicates greater complexity in the solvent than in the adsorbent, which is impossible, when, as in the case of most electrolytes in very dilute solutions, the dissolved body is not merely monomolecular, but almost wholly ionised (*cf.* Walker and Appleyard, *Trans. Chem. Soc.*, 1896, lxix., 1334). The exact physical significance of p therefore remains to be determined, but where the case is one of surface-action $\frac{x}{m}$ is obviously an arbitrary expression, which is proportional for any one adsorbent in a uniform state of division, but gives no indication of the absolute surface involved. Even if the surface is molecular, as it probably is in jellies, we have little knowledge of the perplexity of the molecules. It can hardly be doubted that adsorption is dependent on the same forces as solution, as it is obviously selective and influenced by the chemical relations of the adsorbed and adsorbing substances, and in some cases is a preliminary to actual chemical combination.

(Note.—The exponential character of a curve of experimental results is easily tested by plotting the logs, either natural or common. If the logs of the equation $C_a = \beta C_b^{\frac{1}{p}}$ be taken, we obtain $\log C_a = \log \beta + \log C_b + \frac{1}{p}$. Hence, if we plot the experimental logarithmic concentrations of the solution as abscissæ and those of absorbed substance as ordinates, we shall, if the reaction is rigidly exponential, get a straight line, of which the slope (tangent) is $\frac{1}{p}$, and which cuts the vertical line, passing through the origin $\log C_b = 0$ (or $C_b = 1$) at $\log \beta$. It must not be forgotten in plotting logarithms that in fractional numbers the indices are −, while the mantissæ are always +. Exponential curves rise rapidly at first, but afterwards much more slowly and approximately to a straight line).

Freundlich ("Ueber die Absorption in Lösungen," *Habilitationsschrift*, Leipzig, 1906) has suggested a somewhat different empirical formula from the above for expressing adsorption, the so-called λ formula, in which λ for a given original concentration of the adsorbed solution is constant and independent of the quantity of adsorbent, in which case λ takes the place of β in the simple equation above expressing Henry's law. If, however, the concentration of the solution (*i.e.*, the relation of the dissolved substance a to the volume of the solution v) is varied, $\lambda = a\left(\frac{a}{v}\right)^{-\frac{1}{n}}$, where a and n are constants dependent only on temperature and the nature of the dissolved substance. This formula has been severely criticised by Bain (*Trans. Chem. Soc.*, 1907, xci., 1683), who shows that in some cases it leads to quite anomalous results. Freundlich adopts the view of Lagergreen (*Bihang t. Svenska Vet. Ak. Handl.*, 1899, xxiv., II., Nr. 4, 49; *Zeit. Phys. Chem.*, 1900, xxxii., 174), that adsorption is due to surface-tension, and points out that a dissolved body which lowers the surface-tension between solution and solid must become concentrated on that surface. That this is an actual factor in adsorption admits of no doubt; but our knowledge is not yet sufficient to enable us to calculate its magnitude; and it would seem to imply that adsorption was independent of any direct relation between the adsorbed and adsorbing body, which does not appear to be the case. It may be, however, that chemical relations between the solid and the dissolved substance influence its effect on the tensions of the solid-liquid surface, and so affect the results.

Inorganic sols are frequently coagulated by freezing or evaporation, and this is often really due to the traces of electrolytes always present in the sols, which become concentrated in the remaining liquid till they reach the minimum necessary for flocculation.

Colloid sols are not only flocculated by ions of opposite charge, but by other sols, the two colloids precipitating together in a way which closely stimulates an ionic reaction, and no doubt many of the precipitations, such as those of tannin and gelatin, tannin and basic colours, and basic with many acid colours are of this character. If the two sols are present in exactly the right proportions the precipitation is complete, and the precipitate of almost constant composition; but if one be in excess neither is completely precipitated. Probably in this case, as in flocculation by electrolytes, there is a minimum concentration below which precipitation does not take place.

The cause of this minimum concentration being needed is not clear, but it seems to indicate a certain initial resistance which must be broken down, and which is probably connected with the surface-tension between the particles and the liquid, or possibly with the stability of the electrical double layer, with which the surface-tension is closely connected as shown by the work of Quincke and Lippmann. The resistance to electrolytes is somewhat affected by the rate at which they are added, being greater when the addition is slow or in small quantities than when the necessary amount is added at once.

It can hardly be doubted that flocculation, whether by added electrolytes or by other colloids, is dependent on the neutralisation of the charges of the particles. In the case of electrolytes the ions, of which the charges are much greater than those of the particles, probably act as nuclei round which a number of particles are aggregated. The greater efficiency of polyvalent ions may thus depend on the larger aggregates which their larger charges are able to neutralise, and which naturally fall sooner under the influence of gravity and of cohesive attraction. As the particles probably owe their charges to attached ions, both flocculation and adsorption are in a sense chemical reactions. As one ion probably neutralises many particles the quantity carried down with the gel is relatively very small.

The action of "protective" colloids has been already mentioned, and is usually most marked in the effect of organic colloids on inorganic sols, but certain inorganic sols have also protective effect. Biltz (*Ber.*, 1902, xxxv.,

4431) found that zirconium hydroxide exerted a protective action on gold sols even stronger than that of gelatin; and Ruer (*Ber.*, 1905, xliii., 85), that zirconium and ferric sols containing traces of chlorine gave no precipitate with silver nitrate, the silver chloride remaining in colloidal solution. Kuspert has also produced gold and silver sols by reduction in presence of silica jelly. The efficiency of protective colloids extends to both positive and negative sols, though usually in different degrees, and is marked in a large number of organic colloids, many of which it may be remarked, are amphoteric, and take different charges according to the acidity or alkalinity of the medium. Thus gelatin and its peptones are among the most powerful with regard to gold sols, less than 1 mgrm. being sufficient to protect a litre of gold sol from precipitation by salt, while 80 mgrms. were required to exert an equal protective effect on a (much more concentrated) As_2S_3 sol. Most other colloids are less powerful in their effects, 10 to 20 mgrms. of egg albumen, a somewhat larger amount of gum arabic, and from 0·6 to 2 mgrms. of dextrine or starch being required to produce on gold sol an equal effect to 1 mgrm. of gelatin. Zsigmondy has taken advantage of this difference of effect for the detection and identification of colloids in mixtures (*Zeit. Anal. Chem.*, 1902, xl., 697). He calls the number of mgrms. of a colloid required to protect 10 cc. of a stable gold sol containing 0·0053 to 0·0058 per cent of gold from the precipitating action of 1 cc. of a 10 per cent salt solution the "gold value" of the colloid.

The cause of protective action is not fully explained. It is not due to the viscosity of the colloid, since the effect is produced by quantities too small to have any appreciable influence either on the viscosity of the liquid or the pedetic motion. Neither does it appear due to direct influence on the charges of the particles, since many colloids protect both positive and negative sols. It is more probably due to an actual coating of the particles of the sol with the protective substance. Bechhold ascribes this to surface-tension (*Zeit. Phys. Chem.*, 1904, xlviii., 385). Quincke has shown that in a system of immiscible liquids, A, B, and C, if the sum of the surface-tensions between A—B and B—C is less than that between A—C, B must spread between A and C, forming an intermediate layer (*Ann. Phys.*, 1888, [4], xxxv., 580). Bechhold shows numerically that this is the case in the system mastic-gelatin water, and that the mastic particles must therefore become coated with gelatin, which acts as a protective colloid to a mastic suspension. It is obvious that as the gelatin-coated particles have greater attraction for water and less for each other as compared to mastic they will have less tendency to coalesce. It may also be suggested that the gelatin may form a permanent double layer in the electric sense, which will render the neutralisation of the particles by oppositely charged ions difficult or impossible.

Platinum and gold sols exert a strong catalytic influence similar to that of platinum black and spongy platinum, decomposing hydrogen peroxide, causing combination of oxygen and hydrogen, and other similar effects. These seem merely due to the extended surface and very fine division of the metals, and belong rather to the general theory of catalysis than to that of the colloid state. Metallic sols have, however, been styled "inorganic ferments" from the analogy of their action to that of the catalyses, which are also colloidal, and which bring about similar reactions. Like them the action of the metallic sols is favoured by warmth, and in the case of hydrogen peroxide by small additions of alkali, while larger quantities slow or prevent it. In both cases certain substances, such as hydrogen sulphide and cyanide, exert a "poisonous" or inhibitory effect on the catalyst, which if slight is slowly recovered from. It is doubtful, however, if the resemblance is more than analogy.

The colour of metallic hydrosols is often intense, and varies with their condition, and especially on approaching flocculation; that of silver from dark brown to brown-violet, changing to deep green before flocculation. Gold hydrosols vary from intense red to blue-violet, taking the latter tint before precipitation by electrolytes, though some blue-gold sols are stable. The change of colour does not depend on the average size of the particles, but apparently on their aggregation. Kirchner and Zsigmondy (*Ann. Phys.*, 1904, [4], xv., 573) found that a red-gold sol rendered stable by gelatin becomes blue on evaporation to dryness, and under the microscope shows intensely coloured masses of many submicrons in a colourless medium. On moistening or re-dissolving these become again distributed, and the red colour is restored. Planck (*Ann. Phys.*, 1900, [4], i., 69) has shown that the light absorbed by small particles, which act as "optical resonators" to the electro-magnetic light-wave, must become redder, and that transmitted bluer as they approach each other. Seen in the ultra-microscope the gold particles usually reflect yellow light.

It has been noted that the precipitated gels of inorganic colloids are, in the opinion of the writer, not identical in structure with the true inorganic jellies, but at least in many cases they possess strong points of resemblance, and from their fine state of division retain many colloidal properties, most marked, of course, when they are reversible. They usually retain a portion of water with great obstinacy, so that it has often been mistaken for water of true chemical hydration. In some cases, however, the gels are probably true hydrates, which retain additional water by their surface-attraction. Van Bemmelen, Bütschli, and others have assumed various netted, cellular, and micellar structures in gelatinous gels, and to a certain extent these must have a real existence, though the extension of the theory to the true organic jellies is of doubtful validity. Von Weimarn (*Zeit. Chem. u. Ind. Kolloide*, 1907, ii., 76) has shown that gelatinous precipitates are obtained when concentrated solutions of crystalloids are mixed which react with each other to produce a compound which is very insoluble in the liquid; as, for instance, when concentrated solutions of barium thiocyanate and manganese sulphate are shaken together. These "jellies" may even be perfectly clear and transparent, and consist of drops of one or other solution, surrounded by a thin film of practically colloidal precipitate, which prevents coalescence and further reaction with the surrounding liquid. A very similar effect has been observed by the writer when a concentrated solution of calcium phosphate in hydrochloric acid is mixed with strong ammonia, when the mixture, though smelling strongly of ammonia, may yet contain acid calcium phosphate in excess, which is only slowly decomposed by the diffusion of ammonia into the isolated droplets.* The colloid particles are necessarily extremely insoluble in their media, and whenever precipitation occurs by the mixture of a precipitating solution the gel will be likely to take such cellular forms the dimensions of which will depend on the conditions of precipitation. In other cases where the precipitation is more gradual the particles will still adhere to loose amorphous masses, presenting a very large surface to the liquid, and it is probable that where dilute colloid solutions coagulate in which the surface-tension between the particles and water is considerable they will adhere to a more or less molecular network, which will contract in order to lessen surface and tear into flocculent masses, entangling and carrying down with them, as albumen does, all suspended particles in the liquid. Bütschli ("Untersuchungen über Mikroskop'sche Schäume und das Protoplasma," Leipzig, 1892; Verh. des naturh.-med. Vereins zu Heidelberg, N.F., 1892, v., 28—41, 42—43; 1894, v., 89—102, 230—292; 1896, v., 457—472) found that many gels showed network structures under the microscope with magnifications of about 2000 diams. when suitably treated, and detected similar structure in gelatin when hardened with alcohol or chromic acid; but

* Von Weimarn holds that the sole difference between the colloid and crystalloid condition lies in the extreme insolubility of the minute crystalline elements first formed, which prevents their uniting to form larger crystals, and considers that all matter is potentially crystalline.

as the unhardened gelatin appeared quite structureless it is very probable that the cavities were produced by the hardening process, and it may be noted that gelatin rapidly hardened by dehydrating agents is always more or less opaque and non-homogeneous.

The drying of gels is a continuous process, proceeding rapidly at first with vapour-pressures not materially below that of water, but gradually becoming slower, and the vapour-pressure lower as dryness is approached. Owing to the structure of the gel some time (days or weeks) is required for the mass to reach equilibrium with any definite vapour-pressure. The curve of vapour-pressures as compared with gradually diminishing percentage of water, though continuous, is not always regular, and does not appear to be exponential, and the process is usually irreversible with inorganic gels, or at least partially so, indicating a permanent change of state, though in some cases it may be connected with surface-tension, as in that of swollen gelatin drying in saturated water vapour, which will be mentioned later. Silica-jelly, which was very fully investigated by Van Bemmelen (*Zeit. Anorg. Chem.*, 1896, xiii., 233), may be taken as an example. The fresh gel was dried at a temperature of 15°, at which water has a vapour-pressure of 12·7 mm. in a series of exsiccators containing sulphuric acid diluted to known vapour-pressures until equilibrium was established. The fall of vapour-pressure was at first very gradual, but became more marked at 11 mm. when a water content of 3·7 was reached. (It is not clear from the diagram whether this is 3·7 mols. per mol. of SiO_2, or 3·7 grms. per grm., but probably the former). At a pressure of about 5 mm. and a water content of about 1·5 the gel, which had previously been transparent, became opalescent, and finally procelain-white, and the curve ran horizontally; that is, the vapour-pressure remained constant until a water content of 1 was reached. This constant pressure indicates some change, chemical or physical, which takes place at this pressure, and if the proportions are molecular, might correspond to the decomposition of a definite hydrate, $(SiO_2)_2OH_2$, with a vapour-pressure of 5 mm., or to a change of form to one with lessened attraction for water. The opacity would also correspond to some definite change, as during the horizontality of the curve the gel would be a non-homogeneous mixture of the two substances or two forms. Below 5 mm. the gel again becomes homogeneous and transparent. Van Bemmelen supposes that at this point a further coagulation takes place with contraction of the gel and the production of air-spaces. Up to this point the curve is irreversible; that is, the gel will not absorb moisture in the same way, but only a much lessened quantity in saturated water vapour. Probably in the earlier part of the curve the surface-tension between the water and silica is different from its surface-attraction for water vapour, and the change indicated by the opaque state is not likely to be a reversible one. Below 4 or 5 mm. pressure the drying is a reversible one, and of the character common to all porous or finely divided substances. The drying of ferric hydroxide is very similar in character, but has no marked horizontal in its curve, which is throughout irreversible. From some, perhaps, rather fanciful resemblance of the curves produced to those caused by the hysteresis or "lag" in the magnetisation and demagnetisation of iron, the phenomenon has been described by that name. It produces some curious consequences, of which space does not permit discussion.

Most organic colloids seem to differ somewhat widely from the inorganic sols and gels which have been described, and in many cases their solutions, though possessing colloidal properties, approximate closely to what we should anticipate of true solutions of bodies of the high molecular weights which many of them are known to possess. They present more analogy to emulsions of immiscible liquids which become more miscible at higher temperatures than to suspensions of solid particles like the metallic sols, and have hence been called "emulsion colloids." Their sols usually show the Tyndall effect, and frequently, but not always, submicrons are visible to the ultramicroscope; but both may disappear with rise of temperature or the addition of a "common solvent." They are not usually sensitive to small additions of an electrolyte, and when "salted out" by larger quantities the effect seems often more osmotic than electrical. In some cases, however, when the colloid has acquired a definite positive or negative (ionic) charge it becomes much more sensitive to electrolytes, and where organic sols mutually precipitate each other the presence of a trace of electrolytes is probably essential to communicate the necessary charges. It is stated that gelatin free from inorganic constituents only gives a slight opalescence with tannin, and in ordinary cases the rapidity and completeness of the precipitation are much increased by the presence of salts.

Many aqueous organic colloid solutions are flocculated by additions of alcohol, ether, &c., and, conversely, alcoholic by addition of water, which have usually no action on inorganic sols. These effects are probably purely osmotic and dependent on the solubility of the substance in the different media, but such additions often change the electrical charge of the solvent.

In most cases organic sols are simply viscous liquids which on concentration become more and more viscous till they reach a practically solid form without any break of continuity; but others, usually by change of temperature, pass into the semi-solid state known as jelly. This solidification usually occurs with comparative suddenness, and is sometimes irreversible, but usually jellies have pretty definite melting-points at or slightly lower than their points of solidification, and varying only slightly with the concentration of the solution, but, like the melting-points of fats, not reaching their full value till some time after apparent solidification. Like crystallisation also, the change to the solid form is accompanied by evolution of heat, and liquefaction by its absorption.

Conversely, organic colloids in the solid form are capable of absorbing water or some other solvent, sometimes passing back without break to the viscous condition, but often reaching a maximum absorption and retaining the jelly state. Gelatin, for instance, dissolves direct to a viscous solution at temperatures above 25° or 30°, but swells to a jelly at lower ones, which melts if the temperature is raised. Cellulose and many of its derivatives and many animal and vegetable tissues swell, but do not dissolve without hydrolysis or other chemical change, and may be viewed as irreversible jellies. Thus, dyeing, tanning, and many other industries may be regarded as branches of colloidal chemistry.

The absorption of the solvent is accompanied by swelling or increase of volume, but especially in the early stages by marked contraction of the sum of the volumes of solvent and colloid and considerable evolution of heat; and, conversely, in dehydration heat is absorbed. Consequently, cold promotes swelling (as distinguished from solution), and heat has the opposite effect, though in dilute jellies, which can usually only be subjected to a small range of temperature, these effects are not very marked, and are often masked by other influences such as bacterial fermentation. As an illustration, it may be mentioned that gelatin is most rapidly and satisfactorily dissolved for culinary purposes by swelling in cold water, which may be thrown away with the dissolved impurities, and then melting the swollen jelly by setting the vessel in hot water.

(To be continued).

Notes on Two Methods of Preparing Monomethylamine. — Maurice François. — The author has investigated two methods of preparing monomethylamine, with special reference to the yield and purity of the product. Brochet and Cambier's method with formol and ammonium chloride does not give perfectly pure monomethylamine, and should not be used when purity is specially desired. On the other hand, Hofmann's method by brominated acetamide gives a very pure product, but the yield is comparatively low.—*C. R.*, cxlvii., No. 8.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

PART III.—ANALYSIS OF THE ALUMINIUM AND IRON GROUPS, INCLUDING BERYLLIUM, URANIUM, VANADIUM, TITANIUM, ZIRCONIUM, AND THALLIUM.

By ARTHUR A. NOYES, WILLIAM C. BRAY, and ELLWOOD B. SPEAR.

(Continued from p. 161).

The Iron Group (continued).

Procedure 65*c*.—To the H_2O_2 solution (*P. 65*b*), if coloured, add powdered Na_2SO_3 little by little until the solution is decolorised, and let the mixture stand twenty or thirty minutes. (White flocculent precipitate, presence of *titanium*).

Note.

1. This test serves to confirm the presence of titanium and to enable the quantity of it to be better estimated. H_2O_2 and the sexivalent titanium compound are rapidly reduced by the action of H_2SO_3, even in the cold, and titanium then precipitates as $Ti(OH)PO_4$. As in the case of zirconium, the precipitation takes place slowly. When there was only a faint colour with H_2O_2, no precipitate will be obtained, but 0·5 mgrm. of titanium is easily detected, if the concentration of the sulphuric acid does not exceed 1 cc. H_2SO_4 (1·20) in 25 cc. solution.

**Procedure* 65*d*.—Evaporate the first ether extract (*P. 65*a*) on a water-bath, and dissolve the residue in 3 to 5 cc. H_2SO_4 (1·20) and 3 to 5 cc. water. To the cold solution in a test-tube add 2 to 3 cc. 1 per cent KI solution and powdered Na_2SO_3 a little at a time until the iodine colour has permanently disappeared. (Yellow precipitate, presence of *thallium*). Filter, using preferably a hardened filter when the precipitate is small. Collect a little of the precipitate on a clean platinum wire, and introduce the wire into a colourless gas flame. (Momentary green flame, presence of *thallium*.

Notes.

1. The precipitation of thallium as TlI is practically complete, provided that the volume of the solution is small, say, less than 15 cc. The presence of iron does not prevent a good blank being obtained, nor does its presence in large quantity (500 mgrms.) prevent the detection of 0·5 mgrm. of thallium. TlI is readily oxidised to the soluble TlI_3 by iodine; therefore an excess of sulphite must be present.

2. Any quantity of thallium in excess of 10 to 15 mgrms. is precipitated in P. 11, except when the solution there treated with HCl contains the thallium in the thallic state.

3. The green flame test is a very delicate and characteristic test, but, on account of the volatility of the thallium compound, the green colour is seen only at the moment in which the wire is introduced into the flame. A hardened filter is recommended when the precipitate is small, because the precipitate can be more readily collected on the wire on account of the smooth surface of the filter.

Procedure 66.—Into the ammoniacal solution (P. 64 or P. 65) pass H_2S gas until the mixture after shaking blackens lead acetate paper held above it. (Black precipitate, presence of *nickel* or *cobalt*). Filter and wash the precipitate with water containing a very little $(NH_4)_2S$. (Precipitate, P. 67; filtrate, P. 81).

Notes.

1. In precipitating NiS, the use of H_2S has the advantage that the nickel is all thrown down at once, while with $(NH_4)_2S$ some of it usually remains in the solution, giving it a dark brown colour. If found more convenient, $(NH_4)_2S$ can, of course, be used, the filtrate being boiled to throw down the unprecipitated nickel, as described in P. 51.

2. The filtrate is, in general, tested for the alkaline earth elements, for these may be precipitated with the aluminium and iron groups when phosphate or certain other acid radicals are present, as discussed in P. 51, N. 6 and 7.

Procedure 67.—Transfer the H_2S precipitate (P. 66) with the filter to a casserole, and add 10 to 30 cc. of a cold mixture of 1 volume HCl (1·12) and 5 volumes of water. Digest in the cold for five minutes, stirring the mixture frequently, and filter.

Treat the residue by P. 68.

Boil the HCl solution until the H_2S is completely expelled, add 10 per cent NaOH solution until the mixture is slightly alkaline, transfer to a casserole, cool, and add 0·5 to 1 grm. Na_2O_2 a small portion at a time. Boil for several minutes to decompose the excess of Na_2O_2, and cool the mixture; filter off the precipitate, and treat it by P. 68, uniting with it the residue already obtained in the HCl treatment. Make the solution acid with acetic acid, warm it to about 60°, and pass in H_2S for two or three minutes. (White flocculent precipitate, presence of *zinc*), Apply to the precipitate the confirmatory test as described in P. 57.

Notes.

1. This treatment with dilute HCl serves to extract almost completely the zinc which may be present in this precipitate, owing to its having been carried down in the Na_2O_2 precipitate as described in P. 52, N. 11. A small proportion of the nickel and cobalt present (5 to 20 per cent) always dissolves in the dilute HCl, and the subsequent treatment with Na_2O_2 serves to separate them from the zinc. This separation is satisfactory when, as in this case, the nickel and cobalt are present in such small quantity that only an insignificant quantity of zinc is carried down with them. When therefore the H_2S precipitate is small, it may, instead of being treated with dilute HCl, be dissolved at once in *aqua regia*, and the solution treated directly as described in the last paragraph of the procedure.

2. This procedure must always be followed in order to determine whether or not zinc is present in the substance, except in the case that a satisfactory test for it has already been obtained in P. 57, or in the case that the original Na_2O_2 precipitate (P. 52) was small.

Procedure 68.—Transfer the residue insoluble in dilute HCl, and the Na_2O_2 precipitate (P. 67), with the filters to a casserole, add 5 to 15 cc. HCl (1·12), and a few drops HNO_3 (1·42), warm until the black precipitate is dissolved, and filter off the paper. Evaporate the solution nearly to dryness to expel most of the acid, add about 5 cc. water, and then NaOH solution drop by drop until the mixture is neutral, or until a permanent precipitate just forms. Test one-half of this mixture for cobalt by P. 69, and the remainder for nickel by P. 70.

Procedure 69.—To one-half of the neutral solution (P. 68) add 15 cc. 30 per cent acetic acid, and then 50 cc. 30 per cent KNO_2 solution; dilute to 100 cc., and allow the mixture to stand at least half-an-hour if no precipitate forms sooner. (Yellow, finely divided precipitate, presence of *cobalt*). Filter and wash with KNO_2 solution. If the precipitate is very small, incinerate the filter. Introduce a portion of the precipitate, or of the ash into a borax bead made in the loop of a platinum wire, and heat strongly, adding more of the precipitate or ash if no colour obtained. (Deep blue colour, presence of *cobalt*).

Notes.

1. The yellow precipitate is potassium cobalti-nitrite, $K_3Co(NO_2)6$, which in solution dissociates into K^+ and the complex anion $Co(NO_2)6^{\equiv}$. The precipitate is somewhat soluble in water, but very difficultly soluble in a concentrated KNO_2 solution, owing to the common ion effect of the potassium ion. In the formation of this substance the cobaltous salt is oxidised to the cobaltic state by the nitrous acid displaced from its salt

* From the *Journal of the American Chemical Society*, xxx., No. 4.

by the acetic acid, the cobaltic salt combining as fast as formed with the potassium nitrite, according to the equations :—

$Co^{++}+(NO_2^-)_2+2HNO_2=Co^{+++}(NO_2^-)_3+H_2O+NO$

and—

$Co^{+++}(NO_2^-)_3+3K^+NO_2^-=K_3Co(NO_2)_6$.

2. The formation of the $K_3Co(NO_2)_6$ precipitate takes place slowly, but even when very little cobalt is present (0·1 to 0·2 mgrm.) a distinct test is obtained within ten minutes, but the complete precipitation of a large amount of cobalt requires several hours, so that the method is ill-adapted for the removal of cobalt before testing for nickel. Moreover, when nickel is present, some of it is carried down with the cobalt, and this is true even when the total amount of nickel is small. For these reasons the test for nickel is made in a separate portion.

3. Nickelous salts are not oxidised by nitrous acid, and are not precipitated by KNO_2 except in a very concentrated solution, when a dark yellow to dark red precipitate of potassium nickelous nitrite, $K_4Ni(NO_2)_6$, may separate. By making the volume large, as directed in the procedure, there is do danger of the precipitation of nickel.

Procedure 70.—To the remainder of the neutral solution (P. 68) add 10 per cent KCN solution, a few drops at a time, until all or nearly all of any precipitate that may form at first re-dissolves; then add 0·5 to 3 cc. more (according to the amount of the KCN precipitate). Heat to 50° or 60° in an open casserole, with frequent stirring, for five minutes, or longer if the solution has not become light coloured. Filter off, and reject any small precipitate that may remain. To the filtrate, preferably in a test-tube, add freshly prepared concentrated NaBrO solution (see Note 3) until a piece of filter paper moistened with KI and starch solutions, when dipped into the solution, is coloured blue or brown. Allow the mixture to stand five to ten minutes, and filter. (Brown to black precipitate, presence of *nickel*).

Wash the precipitate; dissolve a small portion of it, if it is large, in 2 to 3 cc. HNO_3 (1·20); add 3 to 5 cc. 10 per cent tartaric acid solution, neutralise with 10 per cent NaOH solution, and add 3 or 4 cc. in excess. Pass in H_2S for about one minute, filter out any precipitate that may form, and saturate the filtrate with H_2S. Filter again if there is a precipitate. (Brown coloration, presence of *nickel*.)

Notes.

1. The reactions involved in the first test for nickel are as follows :—When a little KCN is added to the neutral solution, precipitates of (green) $Ni(CN)_2$ and (dark brown) $Co(CN)_2$ result except when only small amounts of these elements are present. The addition of more KCN causes the precipitate to dissolve owing to the formation of soluble complex cyanides as $K_2+[Ni(CN)_4]^=$ and $K_4+[Co(CN)_6]^{==}$. The complex nickel salt is stable in the air, but the cobalt salt is very readily oxidised according to the equation :—

$$2K_4+[Co(CN)_6]^{==}+O+H_2O=$$

Potassium cobaltocyanide.

$$=2K_3+[Co(CN)_6]^{\equiv}+2K+OH^-.$$

Potassium cobalticyanide.

The first action of the NaBrO is to decompose the excess of KCN, chiefly with formation of KCNO. It then oxidises the nickel to the nickelic state, whereupon the nickel is immediately precipitated as brownish black $Ni(OH)_3$ by the NaOH present. The cobalt, though already in the cobaltic state, is not precipitated as $Co(OH)_3$, because the complex ion, $[Co(CN)_6]^{\equiv}$, is so slightly ionised into its constituent-ions (Co^{+++} and $6CN^-$) that the concentration of the Co^{+++} does not suffice to produce with the OH^- present the solubility-product for the $Co(OH)_3$, and that of the CN^- is so small that it is only very slowly oxidised by the NaBrO.

2. In executing this procedure the following precautions should be observed :—A very large excess of the strong KCN solution over that required to re-dissolve the precipitate should not be added, for the excess must be destroyed by the NaBrO before the nickel can be oxidised and precipitated by it. Yet there must be sufficient KCN added, not only to combine with all the cobalt, but to furnish a moderate excess in order that the oxidation to the cobalticyanide may take place rapidly. Care must also be taken to heat the solution long enough in the air to complete this oxidation, before the NaBrO is added, for otherwise the latter reagent after destroying the free KCN will oxidise the decomposable cobaltocyanide with precipitation of $Co(OH)_3$, just as it does the nickelocyanide; the completion of the oxidation by the air is indicated by the disappearance of the dark colour in the solution. Finally, one must make sure (by applying the iodide-starch test) that an excess of NaBrO over that required to oxidise both the cyanide and the nickel has been added. If these precautions are observed, there is no difficulty in securing a precipitate with 0·2 mgrm. of nickel nor in causing 300 mgrms. of cobalt to remain entirely in solution.

3. The hypobromite reagent is prepared by adding liquid bromine to a known volume of 10 per cent NaOH solution until the solution becomes distinctly red, owing to the presence of excess of bromine, and then adding half as much more NaOH solution. This solution may be filtered through a hardened filter. It decomposes fairly rapidly, with formation of bromate and bromide, and also with evolution of oxygen, and should therefore not be used when more than a few days old. Instead of this reagent, bromine water and NaOH solution may, of course, be used. The concentrated hypobromite solution is recommended because a much smaller volume of it is required to decompose the large excess of cyanide used in the procedure.

4. When an alkaline tartrate solution containing a small amount of nickel (even 0·1 to 0·2 mgrm. in 20 cc.) is saturated with H_2S a clear brown solution is obtained, With somewhat larger amounts of nickel (10 to 20 mgrms.) the liquid is opaque but runs through a filter very readily. The condition of the nickel in this solution is not known. The presence of the tartrate serves merely to prevent the precipitation of $Ni(OH)_2$ by the NaOH solution, owing to the formation of a complex salt containing the nickel in the anion. The brown colour does not appear until the alkaline solution is nearly saturated with H_2S, so that care must be taken to use an excess of H_2S.

5. This confirmatory test for nickel is not interfered with by moderate amounts of other elements of this group, such as cobalt and iron (which, however, should not be present at this point), for on leading H_2S into an alkaline tartrate solution containing these elements, they are completely precipitated as sulphides, and may be filtered off, yielding a filtrate which in the absence of nickel remains clear when saturated with H_2S or becomes dark brown when it is present in even small amounts.

(To be continued).

CORRESPONDENCE.

SULPHATE OF AMMONIA.

To the Editor of the Chemical News.

SIR,—It is now some years since commercial sulphate of ammonia as used for manure contained any appreciable quantity of sulphocyanides. Indeed, the analyst had seldom any reason even to test for the presence of these compounds, for the sulphates of commerce have been so pure as to practically preclude the presence of cyanides. However, for some time past many samples which have come into my laboratory have not been satisfactory as regards colour, and I was induced to make a study of them to determine whether they contained sulphocyanides. In

some cases I found these to be present, but not in so large a quantity as would account for the coloration of the sample. Further examinations revealed the presence of organic compounds the nature of which need not be entered into here, but which in my opinion would be injurious to plant life. It must not be forgotten that sulphate of ammonia in itself is not a direct manure; before it can be utilised by plants it must undergo nitrification. The nitrifying organisms are probably, like most bacteria, susceptible to the influence of organic compounds —coal-tar derivatives—and would therefore be prevented from carrying on their work. These conclusions were not made known to the users in the West Indies of the manure, but they were subsequently confirmed by the managers of the estates, who reported that the manure had failed to give the usual results.

Still further evidence came to show that these compounds were injurious to plant life. It is customary to add a little sulphate of ammonia to the fermenting molasses to supply nitrogen to the yeasts, &c. Gas sulphate of ammonia was found to have very uncertain action and at times apparently an injurious effect on the fermentation. Bone sulphate was therefore substituted, with satisfactory results. It is, however, well known that bone sulphate has a very dark colour, so it was necessary to try and distinguish between the two colouring matters. My assistant, Dr. U. Bonelli, after some work has obtained a simple test. If a grm. of the sulphate is dissolved in 5 cc. water in a test-tube and strong ammonia added, an intense violet coloration is produced where the undesirable organic compounds are present, while no change occurs either with pure gas sulphate or bone sulphate. The detection of sulphocyanides in the presence of these organic compounds is not so satisfactory as in ordinary sulphate of ammonia. We have found the following method give satisfactory results. Five grms. of the sulphate of ammonia are moistened with strong ammonia and then dried in the water-oven. When quite dry the material is ground with 5 cc. of alcohol and the alcohol filtered off. This is diluted with water and tested with ferric chloride, and if sulphocyanides are present the usual bright red coloration is obtained.

I think it behoves all those who are employing sulphate of ammonia as a manure, either alone or as constituent of a compound, to make sure that what they purchase is both free from sulphocyanides and from the organic compounds which give the violet coloration with ammonia. One large firm in the city who are considerable users of this material have decided in future only to accept sulphate which passes these tests.—I am, &c.,

Fredk. J. Lloyd.

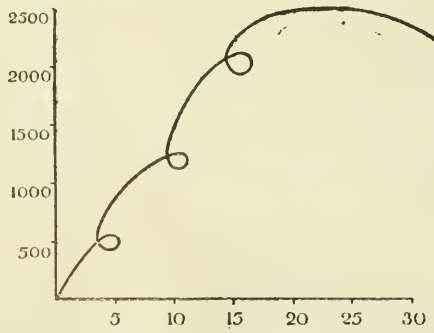
Laboratory,
6, Trinity Square, London, E.C.

WOMEN AND THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

Sir,—In attempting to take a share, however small, in this discussion I am labouring under two disadvantages, viz., (1) my great distance from the centre of disturbance; (2) the fact that I am not a member of the Society. The latter may be, perhaps, more of an advantage after all, as I am able to look quite impartially at the question. I should not have ventured into the field of strife, however, if it had not been for a letter which appeared in your issue of July 31st, signed H. Droop Richmond. I saw at once that Mr. Richmond had discovered the correct point of view from which to study the question, but, unfortunately, he did not fully work out the argument. I have taken the liberty and the trouble to do this to the best of my ability, and now present you with the result.

Mr. H. Droop Richmond's idea, like all truly great ideas, is very simple. Put shortly, it is this:—A woman member of the Chemical Society, by reason of being a woman, would have a better chance of getting her papers read and printed, and thus get a better opportunity for securing a lucrative post than a man. In other words, "the woman chemist would in the long run displace a man, another woman, and their children." Now, suppose 150 women were admitted as members each year. Of course it might be any other number, but 150 will do. These displace 150 men—married men with large families (I follow my authority in this, the "large" family being a sort of bonus); it follows then that these 150 unemployed chemists will not be able to pay their annual subs., and so will cease to be members. Thus each year more women will be admitted, and more *married* men displaced. What will happen? After so many years, say, five, large numbers of weddings will take place withing the ranks of the Society, now composed of only bachelors and spinsters. But these newly-married members will at once come under the law of displacement, so that eventually the Society will be composed entirely of *old maids* (with possibly a few confirmed bachelors). I believe this reasoning is correct; the statistics of the Registrar-General, and of the Chemical Society itself, make the average time of displacement of all married and marriageable members about twenty-five years. After this a reaction would set in, and in about another twenty-five years the Society would have returned to its present condition, and be ready to enter on another



"Droopian" Curve of Membership of the Chemical Society.

Ordinates = Women Members; Abscissæ = Years.

Notice flatness of curve for last seven or eight years, showing reluctance to part with with few remaining men members. The little rings on the curve show the periodic fluctuations caused by epidemic of weddings within the Society—wedding rings, in fact.

cycle. I have traced out a complete cycle of change on squared paper, and send it herewith. I cannot find a curve like it anywhere, so I have christened it the "Droopian." —I am, &c.,

E. G. Bryant.

Port Elizabeth, Cape Colony,
August 21, 1908.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvii., No. 5, August 3, 1908.

New Method of Making Pure Hydrogen.—M. Maurichéau-Beaupré.—When water is added to the product obtained by treating aluminium filings with powdered mercuric chloride and potassium cyanide, hydrogen is evolved, the reaction being accompanied by a gradual evolution of heat. The heat evolved can be used to regulate the rapidity of the decomposition. This method of preparing hydrogen (which may find application in aeronautics) has the following advantages:—It is very simple, the gas is pure, and the yield of hydrogen is very high for a given weight or volume of the metal.

No. 6, August 10, 1908.

Physico-chemical Analysis of Wines.—Paul Dutoit and Marcel Duboux.—The authors have shown that the method of determining electric conductivities, when applied to the analysis of the distillation products of wine, gives better results than acidimetry. Soda is added to the wine, which is then distilled. The curves of neutralisation by hydrochloric acid of the distillate are reproduced in the original paper.

No. 7, August 17, 1908.

This number contains no chemical matter.

No. 8, August 24, 1908.

Methylation in Ethylene Derivatives.—Louis Henry. —The replacement of H joined to C by the group $-CH_3$ in ethylenic glycols and hydrocarbons raises the molecular weight, diminishes the volatility, and raises the boiling-point. With the glycols which constitute the methylation series of ethylene glycol, $(HO)CH_2—CH_2(OH)$, the introduction of the $-CH_3$ group in place of hydrogen lowers the boiling-point. The boiling-points of the methylethylenic hydrocarbons increases regularly with successive substitutions of CH_3 for H. The hydrocarbons are monomolecular both in the liquid and gaseous states, while the hydroxyl compounds are monomolecular only in the gaseous state. The coefficient of association is lower the more completely the hydrogen is replaced by $-CH_3$, and the effect of increase of molecular weight is diminished by the simplification of the molecule $(CH_3—OH)_n$. The hydrochloric ethers are similar to the hydrocarbons, and the replacement of —OH by Cl in the alcohols is accompanied by a considerable lowering of the boiling-point. The oxides also appear to be monomolecular or very feebly associated compounds.

NOTES AND QUERIES.

Potential Energy of the Elements.—I would be sincerely obliged if any reader would afford me the following data for at least three elements, not including H, N, and F:—The quantity of heat in large cal. per grm.-mol. taken up in the change of an element from—(1) A solid state to boiling-point; (2) a solid state to its critical state. Also the density at B.P. and critical state referred to water.—DANIEL J. RANKIN.

Official Methods of American Agricultural Chemists.—Where can I obtain these Official Methods? How are the Bulletins issued, and what is their price?—X.

Rotting Cotton Thread.—I wish to place cotton thread into a solution and dry it so that it may be worked up in a loom along with ordinary cotton into fabric. After it is made I wish to pass the whole through heat or other dry process, so that it will rot away the cotton that has been through the chemical process and leave the ordinary cotton in its proper state. If any reader would kindly give me the names of the chemicals and particulars of working, or tell me where I can obtain the information, I should esteem it a great favour.—J. C. ROLLINSON.

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THE CHEMICAL NEWS.

Vol. XCVIII., No. 2550.

THE FACTORS WHICH INFLUENCE THE RATE OF ALCOHOLIC FERMENTATION.*

By ARTHUR SLATOR, Ph.D., D.Sc.

The transformation of glucose into alcohol and carbon dioxide by the action of yeast is probably not a single chemical reaction but a series of reactions. If one reaction of the series proceeds relatively much more slowly than the others, then the velocity of the transformation is determined by the rate of this slow reaction.

Evidence is brought forward to show that the initial rate of fermentation by living yeast is controlled almost completely by one single reaction. By considering only these initial velocities certain disturbing secondary reactions are eliminated, for change of conditions, which are usually considered to influence the rate of fermentation, have no effect on these initial velocities. The simple laws governing the rate are evidence in favour of considering one reaction to have the control of the velocity.

The rate of fermentation is exactly proportional to the amount of yeast present. The rate of fermentation of the four fermentable hexoses (glucose, fructose, galactose, and mannose) is almost independent of the concentration of the sugar. Glucose and fructose are fermented at approximately equal rates. Yeasts which ferment glucose do not always possess the property of fermenting galactose, and this sugar is fermented only by yeasts which have been grown in the presence of galactose. The fermentation of mannose is similar to that of glucose, but the rates of the two reactions are not equal. The enzyme which ferments mannose seems to be more sensitive to heat than the one which ferments glucose. The influence of temperature on these reactions is almost the same in the case of glucose, fructose, and mannose, but rather less in the case of galactose. These results are most easily brought into accord on the assumption that the enzyme combines with the sugar. Glucose and fructose form the same compound; galactose and mannose form different compounds. It is possible that there exist three different enzymes: glucozymase, which ferments glucose and fructose; galactozymase, which ferments galactose; and mannozymase, which ferments mannose. It is probable that no compound has yet been isolated which can be considered intermediate in alcoholic fermentation. The suggestion that lactic acid is such a compound is of special interest, and has attracted much attention. Lactic acid does not ferment, or ferments only very slowly and incompletely. This is the chief objection to the hypothesis. An intermediate compound must be at least as reactive as the original reagent. The suggestion that lactic acid is liberated in a "nascent state" is considered unlikely, for in constructing the mechanism of other similar chemical reactions such suppositions have not been found necessary.

Fermentation by yeast-juice differs in many respects from that by living yeast. It is probable that the mechanism of the reaction is the same in each case; but the relative rates of the different steps in the two processes are different. The experiments show that there is an essential step in fermentation in which phosphates in some form or another play a part. This reaction proceeds too rapidly in fermentation by living yeast to have any controlling influence on the velocity; but in the fermentation by yeast-juice it proceeds relatively more slowly and influences the rate.

The method of investigating complicated reactions by considering only initial velocities has the advantage that disturbing side reactions are to a large extent eliminated. The method can probably be applied with advantage to other enzyme processes.

* A Paper read before the British Association (Section B), Dublin Meeting, 1908.

COLLOIDAL CHEMISTRY.*

By H. R. PROCTER, M.Sc.

(Concluded from p. 170).

The absorption of water vapour by most solid organic colloids is a cyclical and reversible process, the colloid returning by evaporation to its original condition, and it therefore follows that Clausius's equations can be applied in this case as well as in the expansion of bodies by heat. Rodewald (*Zeit. f. Phys. Chem.*, 1897, xxiv., 193) has done this in the case of starch, and has calculated from the results its internal pressure, which was found to vary from 2073 kilos. per sq. cm. in dry starch to 561 kilos. in starch fully saturated with aqueous vapour. He also calculated from its vapour-pressure its molecular weight in the solid form as 4370, closely corresponding to twenty-seven times the empirical formula $C_6H_{10}O_5$. This is interesting as derived in a different way from the molecular weight determinations in liquids. The method is obviously applicable to other solid colloids.

The pressure exerted in the early stages of colloid swelling are very large, though they become almost inappreciable as the maximum is approached. The ancient use of dry wood wedges subsequently moistened is an instance of this, and it may be mentioned that stones of the trilithon at Baalbec in Syria, weighing over 1000 tons, have obviously been split in this way. The effect has usually been ascribed to capillary contraction, but a little consideration will show that capillarity cannot produce expansive effects. A pile of thin plates (*e.g.*, cover-glasses on the microscope stage) will be compressed and not expanded if water is allowed to be drawn between them by capillarity. The effect is necessarily molecular and osmotic, the liquid getting *within* the sphere of molecular attractions, and so sustaining and liberating for expansion a portion of the enormous internal pressures which have just been mentioned (in the case of starch some 1500 atmospheres).

The point of maximum swelling, whether in liquid or vapour, is obviously a definite equilibrium which is reached when the attraction of the colloid for the liquid or vapour is balanced by the internal attractions of the colloid and the liquid in themselves. The liquid and the colloid are in complete osmotic equilibrium, and consequently, according to a well-known law, are both in equilibrium with the vapour. P. von Schroeder draws attention to an apparent exception to this law, which is of considerable importance, and for which he was unable to offer a satisfactory explanation (*Zeit. f. Phys. Chem.*, 1903, xlv., 75). He found that agar and gelatin jellies swelled to a considerably larger extent when immersed in water than they did in saturated aqueous vapour, and that when the jelly, saturated by immersion, was suspended in saturated vapour, it dried till it was again in equilibrium with the vapour; thus evidencing a greater vapour pressure than the liquid water with which it was in osmotic equilibrium. He found, however, that when the jelly was swollen with an N/100000 solution of a sulphate instead of water, no contraction, but slight further swelling, occurred; while an N/1000000 solution diminished but did not prevent the evaporation. As the N/10^5 solution may be assumed to be completely ionised, it will contain three ions in 2×10^8 cc., and at 0° C. will exert an osmotic pressure of 340 dynes per cm.^{2}. This would involve work of 340 ergs per grm. of water removed, and would correspond to the pressure of a column of water only 0·344 cm. in height, but Von Schroeder took special precautions to avoid difference in level. If, however, a

* A Paper read before the British Association (Section B), Dublin Meeting, 1908.

portion of water is removed from the mass the surface is extended, and work is done (on the assumption of spherical form) of 370 ergs. The surface tension would be less and the osmotic pressure greater, at laboratory temperature (about 365 dynes at 20°), so that the energy of surface tension agrees well with that found to produce the effect, and is a sufficient cause. The figures are perhaps less important as explaining an apparent anomaly than as illustrating the smallness of the forces involved in considerable changes of volume near the maximum swelling. The relation of surface tension to the drying of gels consisting of aggregates of particles, as that of silica, may be here again referred to. If the common tension between the surfaces of the particles is less than that of water itself, as in gels is necessarily the case, they will retain a large amount of water by surface attraction, the vapour pressure of which will be equal to or somewhat less than that of liquid water according to the tenuity of the film. As the water is removed by evaporation the particles will cohere by their mutual attraction, and if this cohesive attraction is greater than the difference between the tension of water and that of the common surface, or, in other words, than the difference between the attraction of the particles for water and the attraction of water for itself, water will not again spread between the particles, and the drying will be irreversible as in the earlier stages of the silica jelly.

The rate of absorption of liquid by solid colloids has been studied by Hofmeister (*Archiv. f. Exp. Path. und Pharm.*, 1890, xxvii., 395), and more recently by Pauli (Pascheles) (*Ibid.*, 1895, xxxvi., 100). The latter showed, both mathematically and by experiment on agar and gelatin, that if Q be the degree of swelling and M its mass, the rate of swelling $\frac{dQ}{dt}$ at any given time is equal to (M − Q)C, the difference between the actual and the maximum swelling multiplied by a constant, which varies with the material, and probably with the temperature. This is a law common to many chemical and physical changes, but complicated in this case by the constantly increasing thickness of the swelling colloid. For very thin plates, where this can be neglected, and between the times t and t_1 and the swelling Q and Q_1 the constant $C = \frac{1}{t_1 - t} \text{ en } \frac{M - Q}{M - Q_1}$, and for agar is about $9{\cdot}5 \times 10^{-3}$.

The swelling of gelatin jelly is much influenced by acids and alkalis, both of which largely increase both its amount and its rapidity. The action of neutral salts on swelling, as regards gelatin, has been investigated by Hofmeister (*Archiv. fur Exp. Path. and Pharm.*, 1891, xxviii., 210; their effect on melting and gelatinising temperatures by Pauli (Pfluger, *Archiv.*, 1898, lxxi., 1), and on viscosity by von Schroeder. All these effects are practically parallel; salts which lesson swelling raise the melting-point of jellies and increase the viscosity of the sols. The effect seems an additive one in which anions and cations take part, but no definite laws have been established. The order of the salts investigated, placing those first which most raise the melting-point, is sulphates, citrates, tartrates, acetates, water, chlorides, chlorates, nitrates, bromides, iodides as anions, and K, Ca, Na, Sr, and Mg as cations, and those placed before water raising and those after it lowering the melting-point. Whether the same order applies to other colloids than gelatin is uncertain, but no doubt the effects depend to a considerable extent on the specific affinities of salt and colloid.

The swelling, though mainly an osmotic effect, is influenced by the solid cohesion of the jelly, and there can be little doubt that at the moment of setting a network is formed, whether molecular or coarser, which remains intact during the existence of the jelly. Experiments made by the writer show that the volume of the jelly at the moment of setting has considerable effect on the maximum of swelling, though concentrated jellies after drying swell in water to more, and dilute to less, than their original volume. A solution originally containing 23 grms. of water reabsorbed 14·5 grms., one of 11 grms. 7·8 grms., and one of 5 grms. 6 grms. per grm. of dry gelatin. If weak jellies are mechanically squeezed a considerable amount of liquid, mostly water, can be expressed, and this has been used as an argument for the cellular (two-phased) structure of jellies. It is obvious, however, that near the swelling maximum this must be possible in any case, since it has been already shown that considerable changes of volume can be produced by changes of osmotic pressure equivalent to less than 1 cm. of water.

The phenomenon of "semipermeability" is frequently exhibited by colloid gels and jellies, and, in fact, all the usual semipermeable membranes are colloidal. Just as solids will dissolve in one solvent, and not in another, so jellies are selective in the liquids which they will absorb. Indiarubber will absorb hydrocarbons but not water; gelatin and agar, water but not hydrocarbons or alcohol; and the process of transfusion in a semipermeable membrane is not one of mere mechanical filtration of a finer order, but of absorption and solution on one side of the membrane, and solution and diffusion on the other, and is intimately connected with the chemical character of the membrane and with its ionic charge. Colloid jellies or membranes are usually impermeable to other colloids, while most dissolved salts diffuse in them with nearly the same rapidity as in pure water, though they are sometimes semipervious to those containing a common ion. In dilute jellies, however, some diffusion of finely divided colloids takes place; and Bechold (x. Vortr. 78, *Vers. d. Naturf. u. Aerzte*, Stuttgart, 1906) has used dilute jellies (under pressure, supported on coarser media) for the fractional filtration of colloid solutions. Gelatin and gelatinous membranes are semipermeable to alcohol, which exerts considerable osmotic pressure in a gelatin-lined cell, and jelly is easily dehydrated in absolute alcohol till it contains less than its own weight of water, very little alcohol diffusing into the jelly. On the other hand, if alcohol is mixed with a warm gelatin solution in insufficient quantity to cause precipitation and is allowed to set, the jelly will show much more than its normal maximum swelling when immersed in water, from the osmotic pressure of the contained alcohol which cannot escape. This observation proves clearly that the contraction is not due to any chemical action of the alcohol, but to simple osmotic causes. If alcohol in sufficient quantity be added to a warm and ungelatinised solution of gelatin, it causes separation of the latter, first as a milky liquid, which rapidly flocculates, and, if stirred, coheres into a solid mass, thus showing all the usual phenomena of coagulation, from what are obviously purely osmotic causes. Similar effects occur with gums, dextrine, and most other water-soluble colloids. With egg-albumen the coagulation is irreversible, but in most cases resolution takes place on again substituting water.

Dilute acids and alkalis greatly raise the maximum swelling of gelatin and all gelatinous animal tissues such as skin. French gelatin with a maximum absorption of seven to eight times its weight of water will absorb over fifty times in hydrochloric acid of 0·003 grm.-mol. per litre, at about which concentration the swelling reaches a maximum, falling gradually to below twenty times at 0·4 grm.-mol. per litre, much beyond which the experiment cannot be carried because of solution of the jelly in the acid. Similar effects occur with all other acids which the writer has investigated in which a sufficient concentration can be employed without causing solution. The concentration of the acid in the swollen jelly is always greater than in the external solution, increasing (in the case of gelatin at least) somewhat rapidly at first, before the maximum of swelling is reached, and later remaining nearly constant at 0·002 or 0·003 mol. per litre above the outside solution; while the total quantity of absorbed acid per grm. of gelatin increases very approximately by an exponential law. The whole of the hydrochloric acid can be estimated by titration with caustic alkali in presence of phenolphthalein, but only a portion with methyl orange, showing that one part of the acid exists in a less ionised

state than the remainder. The swollen jelly can no longer be dehydrated by absolute alcohol, showing that the osmotic pressure of water into the jelly is now greater than that into the alcohol, but a part of the acid, approximately corresponding to that estimated by methyl orange, can be removed by repeated treatment with alcohol. The jelly is still pervious to acid and salt solutions, though probably to a less extent than neutral jelly, and it is obvious that one portion of the acid exists in some sort of combination with the jelly, while another is merely osmotically absorbed. It is clear that no definite conclusions can be drawn until in some way these portions can be distinguished; and as a first approximation (obviously not quite correct) it was assumed that the acid absolved in swelling was of the same concentration as that of the outer solution, the less ionised and more constant portion, which may be called "fixed acid," being ascertained by subtracting the calculated value of the acid in the absorbed liquid from the total found in the jelly. The result showed that the "fixed acid" rapidly reached a maximum coincident with the concentration of maximum swellings, after which it remained approximately constant, a slight downward curve being probably due to the inaccuracy of the assumption that the strength of the absorbed solution was equal to that outside, or, what amounts to the same thing, that the whole of the water in the jelly was present as absorbed outer solution. With a small correction in this sense the amount of "fixed acid" obtained in this way closely corresponds to that not estimated by phenolphthalein, and incapable of being washed out by alcohol. From inspection of the curves it is obvious that that of total acid per grm. of gelatin is of an exponential type, but it is compounded of that of "fixed acid" the character of which strongly suggests chemical combination somewhat complicated by dissociation or hydrolysis, and the curve of swelling, which after its maximum is reached is of a hyperbolic character. If, as is probable from the empirical formula, the molecular weight of gelatin is about 1·800, or its multiple, it would roughly correspond to the fixation of two mols. of HCl by one of gelatin.

The action of salts on unacidified gelatin has been mentioned, and common salt causes a small increase of swelling as compared to water, and even saturated solutions have no dehydrating effect. If, however, salt is added to jelly swollen with hydrochloric acid, swelling is immediately reduced, and very powerful dehydration comparable to that of absolute alcohol is obtained by saturated salt solutions in presence of the amount of acid necessary to the maximum swelling effect. At the same time the total acid in the jelly is diminished, but the "fixed acid" is gradually, though not largely, increased. It is probable that if the concentration of the hydrochloric acid could be increased to an equal extent to that of the salt without causing solution, an equal dehydration would be produced, and it is difficult to resist the conclusion that the swelling is due to the chlorine ion in the acid gelatin, and is osmotically repressed by the increase of the same ion in the solution. Other acids with their neutral salts produce similar effects. The fact that similar dehydration is produced by other acids, *e.g.*, sulphuric, in conjunction with sodium chloride, and probably with other salts, does not contradict the conclusion that it is the common anion which is operative, since in the case suggested an equilibrium of sodium and gelatin sulphate and sodium and gelatin chloride would result. The cause of the general swelling effect of acids must, however, in some way be intimately connected with their common H ion, and that of alkalis, which is equally powerful, with the hydroxyl ion. The alkaline swelling is not repressed by sodium chloride, even when caused by sodium hydrate, but is repressed by sufficient concentration of the hydroxyl ion in the outer solution. The above are the summarised results of a research on which the writer has been some time engaged, and which he hopes shortly to publish with a more detailed discussion of the operating causes. It may be remarked that the dehydration of acidified gelatinous tissues has an important technical application in the preservation of sheep pelts by "pickling" with salt and sulphuric acid, and its bearing on numeral tannages in which salt is employed with alums and other compounds of acid reaction is very obvious. As gelatin is decidedly amphoteric, and is known to be capable of decomposing many salts in solution, it is quite possible that some of the complicated effects of unacidified salt solutions which have been referred to may be due to partial absorption of the acid of the salt and the osmotic effect of the remainder on the compound formed.

Space will not allow of any detailed discussion of the coagulation of the various albumins by heat and precipitating agents, which, important as they are from the physiological aspect, have not yet yielded many facts which can be explained on general principles. Albumins, carefully freed from electrolytes by dialysis, are electrically neutral and incompletely coagulated by heat or by those precipitants which do not at the same time communicate an electrical charge. The addition of a trace of acid which gives a positive charge renders them liable to complete coagulation by heat and much more sensitive to the action of electrolytes; but larger quantities of acid, perhaps by producing soluble acid-albumins, prevent coagulation. Traces of alkalis which give a negative charge have a similar effect, though the precipitation is usually less complete, and excess again prevents or lessens precipitation. Coagulation by heat is usually irreversible, and so also that by alcohol, though zymases are precipitated by the latter in a reversible (soluble) form. Salts of the heavy metals, even in small quantities, produce irreversible coagulation, very possibly connected with combination or colloidal precipitation with a colloidal compound of the metal. Excess of the precipitant frequently prevents precipitation, probably by the formation of new complex compounds. Possibly there may be some connection between these phenomena and the irreversible (tanning) effects of some metallic solutions on gelatinous tissues. These solutions are usually of "basic salts" containing metallic oxides colloidally dissolved. Precipitations of albumins by alkali salts, especially in neutral solution, are generally reversible. (The work of Cohnheim, "Chemie der Eiweisskörper," 1904, and of Pauli and Spiro in the *Beitr. z. Chem. Phys. und Path.* from 1903 onwards seems specially worthy of attention).

The relations of colloid chemistry to technology can here only be briefly alluded to. The industries of india-rubber, gutta-percha, gums, dextrine, glue and gelatin, and cellulose derivatives are of course all colloidal, and it is probable that many reactions which have been described as chemical may really be those of absorption compounds. Tanning and dyeing are particularly concerned with the mutual precipitation of colloids and that by inorganic reagents, and in these industries also the distinction between physical and chemical reactions in any given case is one of extreme difficulty, which is much accentuated by the want of any method for the separation of colloids comparable to crystallisation, or even fractional distillation.

Among industries with inorganic colloids may be mentioned the comparatively new one of the manufacture of colloid fibres for electric glow-lamps from difficultly fusible metals, and both earthenware and agriculture are largely dependent on the properties of colloidal suspensions. Glass manufacture is also a colloid industry, and modern pigments are largely colloidal precipitates and colour-lakes.

In conclusion it is only right to acknowledge indebtedness to the excellent work of Dr. Arthur Müller, "Allgemeine Chemie der Kolloide" (J. A. Barth, Leipzig, 1907), with its extensive bibliography; and to the *Zeitschrift für Chemie und Industrie der Kolloide*, edited by Dr. Wolfgang Ostwald, without which the preparation of such a report would have been extremely laborious. Owing to the very numerous and often somewhat inaccessible journals in which important work has appeared, it has been necessary in many cases to trust to abstracts, and it is possible that from this cause full justice has not been done to some authors.

THE INDESTRUCTIBILITY OF MATTER AND THE ABSENCE OF EXACT RELATIONS AMONG THE ATOMIC WEIGHTS.

By DANIEL F. COMSTOCK.

The two chief reasons briefly stated for believing in the evolution of the elements one from another are, first, that some such process is undoubtedly taking place in the case of the radio-active substances, while we are being forced toward the conclusion that all the elements are radio-active to some degree; and, second, that in the hottest stars only two known elements occur, namely, hydrogen and helium, while as we pass successively to cooler and cooler stars the other elements gradually make their appearance in a more or less orderly manner. Apparently this can only mean that at these transcendental temperatures the forces due to molecular or atomic impact are comparable with the interatomic forces involved in the breaking up of one element to form another, and hence the combination necessary for the formation of the heavier elements can take place only after the temperature has sufficiently dropped.

There is one seemingly fatal objection, however, to any very simple statement of the evolutionary theory, and this objection has not been sufficiently emphasised. The difficulty is this, that so far as we know there are no exact simple relations between the various atomic weights, whereas if we are to assume, as the simplest form of the evolutionary theory does, that the lighter elements come from an atomic disintegration of the heavier ones, or *vice versâ*, it is evident that simple additive relations must exist.

As we know, many simple additive relations do exist, but they are approximate, not exact, and the deviations from exactness, though small, are larger than we can explain from error in atomic weight determinations.

On the basis of common conceptions, therefore, the evidence seems contradictory, certain facts seeming to require the simple evolutionary idea, while another fact, the inexactness referred to above, seeming to deny it.

I wish to show that on the basis of the electrical constitution of matter this inexactness is not only to be explained but it is to be expected.

By the electrical constitution of matter is meant merely that conception, which has grown in favour among physicists of late, which considers the atom to consist wholly or in part of a group of electric charges. Some of these make themselves evident in an ionised electrolyte, or in a gas, but in general the fact tbat the two electricities, positive and negative, are present in equal amounts makes the atom neutral as regards action on an outside point.

Now, since moving charges always act like currents, and hence must set up magnetic fields, it must follow that when an apparently uncharged atom is set in motion there will be set up inside of it a magnetic field, which depends for its strength and distribution on the number, position, and magnitude of whatever charges the atom may be supposed to contain. It will therefore require more energy to set the atom in motion because of the necessity of building up this field, and hence the atom will have an added inertia, *i.e.*, an added mass because of these charges.

Now, it has been shown mathematically by the author (*Phil. Mag.*, Jan., 1908), without making any assumption as regards the structure of the atom, that *this added mass due to the electric charges is strictly proportional to the total electrical energy contained in the atom.*

By electrical energy is meant the energy which we know must exist in space wherever there are electric lines of force. Two charges, one positive and one negative, attract each other, and if these are separated to a distance, work must be done against their mutual attraction. Since the charges themselves have changed in no way, the energy put in must exist in the surrounding space in a form generally known as "strain in the ether." Magnetic lines of force also correspond to energy stored in space, and the statement proved in the paper mentioned above is that the added mass which an atom possesses because of the electric charges which it is supposed to contain depends only on the total electric and magnetic energy which the atom contains, and is directly proportional to this energy.

The expression found may be written—

$$M = \frac{4}{3}\frac{E}{V^2},$$

where M is this "electric mass," V is the velocity of light, and E is the total contained electromagnetic energy of the kind described above.

The amount of energy which corresponds to a grm. mass is enormous. It is readily calculated from the formula, and is found to be 7×10^{20} ergs, approximately, so we may make the statement that, on the present bases, *the inertia of a grm. mass is due to the existence within it of* 7×10^{20} *ergs of confined energy.*

Now, when the atom of an element breaks up the process is a violent one and a large quantity of energy is lost, *i.e.*, goes ultimately into heat. Hence, if this electric energy lost—and on the basis of the electrical conception it *is* electrical energy—it follows from the above that *there must have been a loss in mass accompanying the atomic disintegration* because of the energy lost. Hence, taking the simple case of an atom of A, splitting up violently, and forming atoms of the elements B and C, we would find that the mass of B and C, taken together, would be a little less than the mass of A, from which they came, the difference corresponding to the loss of mass accompanying the loss in energy.

Now, the loss of energy when an atom of radium breaks up is known, and calculation shows that this would give a loss in mass which would be of about the same size as the deviations in atomic mass or weight so common in the table.

In an important paper, Rydberg (*Zeit. Anorg. Chem.*, 1897, xiv., 66) has shown that the atomic weights of the first twenty-seven elements of the periodic system approximate to whole numbers very much more closely than chance could bring about. He has also shown that the atomic weights of these elements are best considered as the sum of two parts (N + D), where N is an integer and D is a fraction, in general positive and smaller than unity. If M is the number of the element in the system (called by Rydberg the "Ordnungszahl"), then N is equal to 2M for the elements of even valence and 2M + 1 for the elements of odd valence. The accompanying table shows the various quantities. I have used, however, the International Atomic Weight values for 1907 instead of those Rydberg used.

Many besides Rydberg have, of course, noticed and studied the curious deviations in the table of atomic weights, and Rydberg's work is mentioned merely because it seems unusually explicit.

The orderly arrangement of the series is striking. It will be noticed that in three cases only are the D's greater than unity, and only in two cases are they negative.

Rydberg points out that although the heavier elements do not conform well to this scheme, *i.e.*, do not in general give the small fractional values of (D) noticed above, yet this is in reality no valid objection, for the numerical values of the weights of heavier elements depend much more on the value of the arbitrary unit chosen than do those of the lighter weight elements, and hence they can have little influence one way or the other in estimating the validity of the curious relations he sets forth.

The whole question is, of course, whether these differences represent real physical deviations from something, or whether they are merely mathematical remainders. Rydberg certainly believes them to represent physical realities, and considering the before-mentioned overwhelming improbability that the approximation of the atomic weights to whole numbers is due to chance, we can hardly doubt that he is right.

Sign.	M.	N. 2M.	N. 2M+1.	Atomic weight.	D.
He	2	4		4	
Li	3		7	7·03	0·03
Be	4	8		9·1	1·1
B	5		11	11·0	0
C	6	12		12·00	0
N	7		15	14·01	−0·99
O	8	16		16·00	0
Fl	9		19	19·0	0
Ne	10	20		20·0	0
Na	11		23	23·05	0·05
Mg	12	24		24·36	0·36
Al	13		27	27·1	0·1
Si	14	28		28·4	0·4
P	15		31	31·0	0
S	16	32		32·06	0·06
Cl	17		35	35·45	0·45
A	18	36		39·9	3·9
K	19		39	39·15	0·15
Ca	20	40		40·1	0·1
Se	21		43	44·1	1·1
——	22	44		—	—
——	23		47	—	—
Ti	24	48		48·1	0·1
V	25		51	51·2	0·2
Cr	26	52		52·1	0·1
Mn	27		55	55·0	0·0
Fe	28	56		55·9	−0·1

The question will doubtless be asked why there is no loss of mass found when a violent chemical reaction takes place and energy is lost. The expression for loss of mass in terms of loss of energy, when written in the differential form (substituting $V = 3 \cdot 10^{10}$), is—

$$\Delta M = \frac{4}{27} 10^{-20} \Delta E,$$

and if we substitute the heat of reaction of any known chemical reaction for ΔE, we find that ΔM is too small to be detected even by the delicate experiments of Landolt.

For the reaction $O_2 + 2H_2 = 2H_2O$, ΔM for 1 grm. molecule is about 10^{-10} of a grm.

In radio-active changes, however, the energy is enormously greater, and hence is to be detected as before mentioned.

If we consider the whole atom is electric instead of only part, as we have considered above, a conception which is by no means artificial, since it has been proven that the mass of an electron is entirely due to its charge, we reach the interesting conclusion that on this basis the "Indestructibility of Matter" is only a corollary of the "Conservation of Energy," for if the atoms are to be considered as electrical systems, it follows that the law of the Conservation of Mass, which is essentially the same as the Indestructibility of Matter, must be approximately true, though not strictly true. It must be approximately true because no known chemical or physical change, with the exception of radio-activity, involves anything but a relatively minute liberation or absorption of energy, but the law cannot be absolutely exact, for even this minute loss of energy must involve, on the present basis, its corresponding loss of mass. Thus even the cooling of a hot body must involve a certain diminution of mass, though this, of course, is extraordinarily small, much smaller even than the loss due to most chemical reactions.

It would be interesting to search for other evidence of the existence of this vast store of energy in matter. Such evidence would involve effects which would be approximately proportional to the density. Such an effect is found in the case of the absorption of the β-rays of radium when passing through different kinds of matter. Here the absorption is proportional to the density over a very wide range. Strutt has shown that in the case of fourteen substances, whose absorption he measured, where the density varied from 0·007 in the case of sulphur dioxide to 21·5 in the case of platinum, the ratio of the absorption to the density has an average deviation of only 20 per cent.

From a physical point of view, also, it is interesting to note that, since gravitation has always been found to b strictly proportional to mass, it follows from the above that the electrical structure of matter requires that gravitation should be proportional to the energy contained in the gravitating bodies, and to this energy alone. Thus, gravitation must be considered on the present basis as existing between quantities of confined electromagnetic energy, and not between "masses" in any other sense. More knowledge bearing on the electrical theory of matter would therefore throw considerable light on the outstanding mystery of gravitation.

Summary.

We have seen that, assuming the electrical theory of matter—the theory, that is, which considers the atoms as systems composed of electric charges—it follows that the mass of a piece of matter is determined solely by the amount of electromagnetic energy which it contains and is proportional to this amount. The energy in ergs which endows 1 grm. with its mass is equal to three-fourths of the square of the velocity of light, or, in round numbers, twenty million horse-power-hours, or the energy corresponding to the work of one thousand horses working for two years. This enormous amount is by no means impossible, since the amount of energy which the radio-active substances are known to *lose* in passing to lower forms is quite appreciable in comparison.

On the electrical theory of matter it therefore follows that the chief property of matter, the property which gives us a quantitative definition, namely, its inertia or mass, is really a property of the energy stored up within the structure which defines the space relations of a piece of matter, and is not a property of the structure itself. Thus it follows that the law of the "Conservation of Mass," which we have here reason to believe is only approximate, is in reality a corollary to the law of the "Conservation of Energy," and thus this latter law and the "Indestructibility of Matter" are closely akin.

From the above it follows that on the present basis any loss of energy must involve a decrease in mass. Thus when a chemical reaction which liberates heat has taken place, when a body is cooled, or when by the process of radio-activity one substance loses energy and is transformed into another substance, there must be a decrease in the mass of the whole, and hence also a decrease in weight. In the first two cases mentioned, however, the change is too small to be detected, but in the last case the change should be appreciable, and we have a ready explanation of the irregularities which occur in the table of atomic weights.

Finally, it is pointed out that since gravity is proportional to mass it would appear that gravitation must be considered as acting between quantities of confined energy, and not between "masses" in any other sense.—*Journal of the American Chemical Society*, xxx., No. 5.

Action of Arsenic Chloride and of Arsenic on Cobalt.—F. Ducelliez.—When arsenic chloride acts on cobalt it transforms the metal into a chloride, and simultaneously an arsenide is formed. The composition of this arsenide varies according to the temperature, the limits being expressed by the formulæ $CoAs_2$ and Co_3As_2. Mixtures of arsenic and cobalt heated in hydrogen to constant weight yield the same series of arsenides. The latter compound, Co_3As_2, can also be prepared by the reduction at 900° of cobalt arsenite or arsenate by means of hydrogen. None of the cobalt arsenides are attracted by a magnet. Chlorine, oxygen, and sulphur react energetically with them; aqua regia and nitric acid dissolve them readily; hydrochloric and sulphuric acids have but little action on them; the alkalis and alkaline carbonates attack them slowly when they are fused together.—*Comptes Rendus*, cxlvii., No. 8.

SOME OBSERVATIONS ON THE ASSAY OF TELLURIDE ORES.

By GEORGE BORROWMAN.

MUCH has been written concerning the assaying of telluride gold and silver ores, yet the literature affords striking contradictions as well as statements unsupported by experimental data. However, there seems to be agreement in the opinion that tellurium is the cause of serious irregularities. Mr. A. L. Davis, in *Tech. Quart.*, vol. xii., sums up the situation as follows:—"As to the percentage of loss sustained in work, whether by scorification or crucible method, many experiments carried out upon the foregoing lines indicate to me that nothing definite can be laid down in regard to it. Every ore, every slag, every scorification, every cupel, let alone the temperature at which the assay is carried on, has some effect upon the loss, and these make too many unknown quantities to arrive at any conclusion."

It was the purpose of the writer in the work here recorded to ascertain a few facts concerning the effect of tellurium in the crucible assay for gold. The points investigated were: loss in the slag; loss in cupellation; the effect of variation in temperature of fusion.

The ore selected for the experiments was a high-grade telluride gathered from various parts of Colorado, rich in silver, gold, and tellurium. With the sulphuric acid test it gave a very strong indication of the latter element, and analysis showed the presence of 10·5 per cent chiefly as hessite and sylvanite. The gangue was silicious, consisting of quartz, felspar, and a little calcite. The ore had a reducing power of about 1·5.

The material was ground very fine, first through 120 mesh sieve, then in agate till all passed through bolting cloth. In all the work 1/10 A. T. was taken for each assay, the samples being weighed out on a quantitative balance instead of on the usual pulp scales. All fusions were made in a muffle at about 1200° excepting in Series No. 4; all the fluxes were passed through a 40-mesh sieve mixed with the ore till thoroughly homogeneous. In short, the greatest care was taken to eliminate all variations except the one studied.

Experiments were first conducted to learn the influence of tellurium in carrying gold into the slag. Mr. C. H. Fulton (*Journ. Am. Chem. Soc.*, xx., 586) records data to show that slag losses in telluride fusions are much greater than in ordinary gold ore crucible work. Messrs. Hillebrand and Allen (*Bull.* No. 253, *U.S. Geological Survey*) find losses insignificant, and commenting on the work of Mr. Fulton suggest that his losses might have been due to the use of iron nails in the fusions.

In the investigation of this point a series of assays was first made on the raw ore, using the following charge:—

Ore 1/10 A.T.	
Litharge	90 grms.
Silica..	10 ,,
Argols	2½ ,,
Sodium bicarbonate	30 ,,
Salt cover.	

Another series was then made on ore from which the tellurium had been removed. In removing it use was made of the fact that nitric acid dissolves tellurium and silver in a telluride and leaves the gold in the residue. Each sample was boiled with nitric acid (1·27) till no further action was apparent; the residue was washed and dried and fluxed under the same conditions as maintained in the first series. Enough silver was added to the detellurised series to replace what had been removed by the acid. The slags from each series were then carefully ground and assayed, using the following charge:—

Slag	
Litharge	30 grms.
Argols	2 ,,
Salt cover.	

The buttons from both the ores and slags were cupelled. The results are set down in the following tables:—

SERIES No. 1.

No.	Ore. Mgrms. gold found.	Ore. Ozs. gold per ton.	Slag. Gold found.
1.	16·14	161·4	None
2.	16·18	161·8	,,
3.	16·18	161·8	,,
4.	16·23	162·3	,,
Average.	16·18	161·8	

SERIES No. 2.

1.	16·10	161·00	Trace
2.	16·16	161·60	None
3.	16·20	162·0	Trace
4.	16·11	161·10	None
Average.	16·14	161·4	

From the above data it is obvious that the influence of tellurium in carrying gold into the slag is very slight, if there is any; the amount recovered was in no case weighable.

The effect of tellurium in cupellation was next investigated, and incidentally the functions of litharge in the fusion. On the assumption that the tellurium in a crucible charge is oxidised by the litharge and carried into the slag, a series of charges was made up varying this constituent from 90 to 180 grms. Theoretically the amount of tellurium carried into the button as a lead alloy should be in inverse ratio to the amount of litharge in the fusion. A series of four samples was made in duplicate. The buttons of one series were dissolved in nitric acid and the tellurium determined by precipitating it in hydrochloric acid solution with sulphur dioxide. The other series was cupelled for gold. The two duplicates are considered as one series, *i.e.*, No. 3.

SERIES No. 3.

No.	PbO in charge. Grms.	Te in button. Mgrms.	Gold found. Mgrms.	Gold per ton. Ozs.
1.	90	lost	16·10	161·00
2.	120	287·5	16·24	162·24
3.	150	298·9	16·18	161·80
4.	180	176·8	16·15	161·50
Average			16·17	161·70

All of the beads of the above series were frosted, showing the presence of tellurium, notwithstanding the great excess of litharge in the fusion. It would then seem that litharge in reasonable amount is inadequate to slag off all the tellurium in this ore. The loss of gold, however, was inconsiderable, the average of the series varying but 0·01 mgrm. from the average of Series No. 1 in which the tellurium had been removed previous to fusion. These results are at variance with published statements regarding tellurium in cupellation. Messrs. T. J. Eager and W. W. Welch, however, found that no loss occurred in the presence of the element up to 10 per cent. The amounts in the above experiment are many times that. A bead from an assay, duplicate of No. 1 in the above series which was also the same as those of Series No. 2, was tested quantitatively for tellurium and 6·9 mgrms. were found; so that it may be present even in the bead in considerable amount without there being more than a negligible loss of gold.

The work was concluded with some experiments to learn the effect of variation of temperature of fusion on gold recovered and the amount of tellurium carried into the button. Some assayers recommend an extremely high temperature. Mr. R. W. Lodge, however, in his "Notes on Assaying," states that he believes high temperatures break up some tellurium compounds in the slag with a consequent alloying of the element with the lead.

A series of four was run in duplicate consisting of charges made up exactly as those of Series No. 2. The tempera-

ture was varied between 800° and 1600°. As in the previous experiment the buttons from one set were cupelled for gold, the other dissolved in nitric acid and assayed for tellurium.

Series No. 4.

No.	Temp. ° C.	Weight of buttons.	Gold found. Mgrms.	Gold per ton. Ozs.	Tellurium found. Mgrms.
1.	800	30·5	16·10	161·00	258·2
2.	1000	32·5	16·16	161·60	150·0
3.	1250	32·8	16·20	162·00	195·6
4.	1600	32·8	16·16	161·60	215·9
Average			16·16	161·60	

The irregularities in the amounts of tellurium could not be accounted for, yet it seems improbable that the amount varies directly with the temperature. As to the gold the yield is greatest at about 1200°, though the average of the series is but slightly below that of Series No. 1.

Summary.

The foregoing data seem to warrant the conclusion that tellurium as the cause of irregularities in crucible work has been overestimated. Slag losses are no greater than in ordinary gold ores; the element may be present in the lead button in relatively large amounts with no considerable percentage of loss. The presence of tellurium in the bead does not necessarily imply a loss of gold in the cupellation, though, of course, a frosted bead would not be permissible when silver is to be determined. In high-grade tellurides when silver is to be estimated, the writer suggests a preliminary treatment with nitric acid, with subsequent precipitation of the silver as chloride, which may be dried and added with the residue from the acid treatment to the fluxes in the crucible. Variation in temperature of fusion does not seem to be of great moment, though the data above are most favourable to a temperature of about 1200°.

The average obtained from Series No. 1 is higher than that obtained in the others, showing a loss due to tellurium in fusion and cupellation, yet the variation is small, the average of No. 1 being not more than 0·24 per cent higher than the lowest average, that of Series No. 2. The members of the various series differ among themselves in some cases considerably, but perhaps not more than would be expected in any high-grade ore, owing to lack of homogeneity of sample. In the opinion of the writer, irregularities in high-grade tellurides are due more to this lack of homogeneity than to tellurium. It is conceivable that in some ores the ratio of gold to tellurium might be much less and hence the percentage of loss greater. In such cases a preliminary treatment with nitric acid to remove the tellurium would obviate the difficulty. — *Journal of the American Chemical Society*, xxx., No. 6.

A CHARACTERISTIC TEST FOR HIPPURIC ACID.

By WILLIAM M. DEAN.

Hitherto no easily-applied, characteristic test for hippuric acid in urine has been at hand. For the reason that its detection in urine is of little or no clinical value, the lack of a convenient practical method for its detection has not been felt. On the other hand, for purely scientific purposes, the methods now in use involve inconveniences that are surprisingly great when compared with the methods available for the detection of other constituents of urine. As a matter of fact, the detection of hippuric acid has necessitated the concentration of the urine, the extraction with organic solvents, and either a melting-point determination of the residue, or its transformation into more easily recognised nitro or benzaldehyde derivative. (Spiro, *Z. Physiol. Chem.*, xxviii., 117; for quantitative methods, *vide* Wiener, *Arch. exp. Path. Pharm.*, xl., 314; Blumenthal, *Chem. Centr.*, 1900, II., 447).

The following test for hippuric acid can not only be applied directly to urine, but it yields definite results in solutions so dilute even as hundredth-normal. A few cubic centimetres of the urine in a test-tube are first treated with a quantity of sodium hypobromite solution, just sufficient to decompose the urea and to impart to the mixture a permanent yellow colour. The solution is then heated to boiling; an orange or brown-red precipitate is formed, if hippuric acid is present. When present only as a trace the solution appears smoky and faintly red in colour; when present in larger quantities the solution is rendered opaque and orange or brown-red in colour. In either case after standing for some time the solution clears up and a light, finely divided precipitate settles. It consists of white "earthy phosphates" intermixed with the amorphous orange or brown-red solid about to be described. (Application of the hypobromite test to aqueous solutions of other constituents of urine gave no colour effects. The following were tested:—Uric, benzoic, oxalic, and fatty acids, creatinine, acetone, acetacetic ester, glucose, glycogen, and leucine).

When a 0·1-N solution of hippuric acid is boiled with the sodium hypobromite solution, a deep brown-red colour is formed at once, and on standing settles to the bottom of the tube as an opaque, red, closely-adhering scale, which cannot be washed from the tube by simple decantation with water. With 0·01 N or even more dilute solutions, the red, adhering mass is easily observed when the liquid contents of the tube are removed.

It must be remembered that continued boiling decomposes the substance, thereby giving rise to phenylisocyanide and other products. For this reason the red substance is best prepared as follows. A concentrated solution of sodium hippurate is prepared and treated at ordinary temperatures with the hypobromite solution. After a few moments the mixture becomes red and after a few hours the precipitation is complete. It is free from the odour of phenylisocyanide and appears as a sticky, blood-red, semi-solid substance. It is insoluble in water but is soluble in most organic solvents. Its alcoholic solution is easily precipitated by the addition of water. Its solution in carbon bisulphide darkens and on evaporating leaves a green-black precipitate.

The substance contains carbon, hydrogen, nitrogen, and bromine. Limpricht and Uslar (*Ann.*, lxxxviii., 133) heated hippuric acid to 240°—250° and obtained benzoic acid, benzonitrile, and resin. With sodium hydroxide and chlorine, Stecker (*Ann.*, lxviii., 54) and Gössmann (*Ann.*, xc., 181) obtained benzoylglycollic acid. The red substance obtained is not analogous to any of these. Its composition and the action of sodium hypobromite on benzamide, *p*-phenylenediamine, and other nitrogen and hydroxyl aromatic compounds is being investigated.— *Journal of the American Chemical Society*, xxx., No. 9.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

Part III.—Analysis of the Aluminium and Iron Groups, including Beryllium, Uranium, Vanadium, Titanium, Zirconium, and Thallium.

By ARTHUR A. NOYES, WILLIAM C. BRAY, and ELLWOOD B. SPEAR.

(Continued from p. 172).

Test Analyses.

Numerous analyses were made to test the efficiency of the process above described. Nearly all of those which were made after the procedure assumed final form are reproduced in the tables. Almost all the analyses relating to the common elements alone were made before the procedures for the rare elements had been worked out, but the process

* From the *Journal of the American Chemical Society*, xxx., No. 4.

T. A. No.	114	115	116	117	118	119
Mn	10 S	2 S	1 S	500 S	500 S	0 S (*d*)
Al	10 S	2 S	1 D (*a*)	0 D (*a*)	2 S	0 D (*a*)
Cr	10 S	2 S	1 S	0 S	2 F (*c*)	0 S
Zn	10 S	2 S	1 S	0 S	2 S	0 S
Fe	10 S	2 S	1 S	0 S	2 S	500 S
Ni	10 S	2 S	1 S	0 S	2 S	0 S
Co	10 S	2 S	1 S	0 S	..	0 S

T. A. No.	120	121	122	123	124	125
Mn	500 S	500 S	100 S	1 S	..	..
Fe	0 S	1 S—	1 S	100 S	500 S	500 S
Ni	2 S	1 S	..	..	3 S	1 S—

T. A. No.	126	127	128	129	130
Co	0 S	0·5 S	150—	150—	150—
Ni	250—	250—	0 S	0·3 S	0·15 S

T. A. No.	131	132	133	134	135	136
Al	0 S (*b*)	0 S (*b*)	0 S (*b*)	0 S (*b*)	0 S (*b*)	0 S (*b*)
Cr	2 S	1 S	0 S	..	0 S	1 S
Zn (In P. 57)	2 F	4 F	10 F	20 S— (*e*)	5 F	0 S
Zn (In P. 67)	2 S	4 S	10 S	20 S	5 S	0 S
Mn	500 S	500 S	500 S	500 S	0 S	2 S
Fe	0 S	0 S	0 S	0 S	500 S	500 S
Ni	0 S	0 S	0 S	0 S	0 S	2 S

T. A. No.	137	138	139	140	141	142	143
PO_4	..	..	..	..	..	200 S	200 S
Zn (In P. 57)	5 F	5 S (*g*)	10 S— (*f*)	3 F	5 S— (*e*)	5 F (*h*)	10 F (*h*)
Zn (In P. 67)	5 S	5 S	10 —	3 —	5 —	5 —	10 S
Fe	500 S	500 S	500 S	..	..	..	..
Ni	..	..	..	250—	250—	250—	250 S
Co	..	..	..	250—	250—	250—	250 S

T. A. No.	144	145	146	147	148	149
Al	0 S (*b*)	3 S	3 S	0 S (*b*)	0 S (*b*)	0 S (*b*)
Cr	0 S	2 S	1 S	1 S	0 S	10 S
Zn (In P. 57)	0 S	5 S— (*e*)	3 F	3 S—	3 F	20 S— (*e*)
Zn (In P. 67)	0 S	5 S	3 S	3 S	3 S	20 S
PO_4	0 S	200 S	200 S	100 S	100 S	100 S
Fe	500 S	500 S	500 S	100 S	100 S	100 S
Ni	0 S	2 S	1 S	0 S	..	..
Co	0 S	2 S	1 S	0 S	100 S	100 S
Ba	0 S	2 S	1 S—	0 S	0 S	0 S
Ca	0 F (*i*)	0 F (*i*)	0 F (*i*)	4 S	0 F (*i*)	100 S
Mg	0 S	2 S	1 S	2 S	2 S	100 S

T. A. No.	150	151	152	153	154	155
Cr	2 S	..	0 S	..	2 S	1 S (*k*)
Zn (In P. 57)	3 F	5 S	0 S	1 F	..	..
Zn (In P. 67)	3 —	5 S	0 S	1 S	..	..
PO_4	100 S	100 S	..	..	..	..
Fe	100 S	100 S	0 S	..	..	..
Co	100 S	100 S	500 S	500 S	..	..
Ba	2 S	1 F	..	..	100 S	100 S

T. A. No.	156	157	158	159	160	161
Cr	0 S	0 S	2 S	1 S (*l*)	..	..
U	100 S	0 S	100 S	100 S	100 S	1 S
V	0 S	100 S	100 —	100 —	1 S	100 S

T. A. No.	162	163	164	165
Al	500 S	500 S	1 S	1 S
Be	0 S	2 S (*m*)	0 S	100 S

T. A. No.	166	167	168	168*a*	169	170
Zn	..	..	..	..	200 —	200 S
Al	200 —	200 —	..	..	..	200 S
Be	..	..	50 —	50 S	..	..
U (In *P. 58*c*—*d*)	2 F	3 S—	2 F	2 S—	2 S	2 F
U (In *P. 58*h*)	2 —	3 —	2 —	2 S—	2 S—	2 S

T. A. No.	171	172	173	174	175	176
Al	..	..	..	..	..	200—
Mn	..	..	..	..	..	200 S
Fe	500 S	500 S	0·5 S	500 S	500 S	200 S
Ti	0 S	1 S	5 S	..	..	..
Zr	0 S	1 S	..	..	..	..
Tl	0 S	..	..	1 S	0·5 S	1 S (*n*)

T. A. No. Begun at—	177 P. 52	178 P. 51	179 P. 51	180 P. 52	181 P. 51
Cr	2 S	1 S— (*p*)	1 S	1 S	2 F (*o*)
U	3 S	1 F (*q*)	1 F (*q*)	0 S	100 S
V	3 S	1 S	1 S	0 S	100 S (*x*)
Zn (In P. 57)	3 S	1 F	1 S	1 F	100 S (*y*)
Zn (In P. 67)	3 D	1 S—	..	S—	S
Al	3 S	200 S	1 S (*r*)	0 S	0 S
Be	3 S	1 S	0·5 S	0 S	0 S
Mn	3 S	1 S	1 S	200 S	300 S
PO_4	..	..	..	320 S	..
Fe	3 S	200 S	1 S	1 S (*s*)	1 S (*t*)
Ti	3 S	1 S	0·5 S	1 S	0 S
Zr	3 S	1 S—	1 S	1 F (*z*)	0 S
Ni	3 S— (*u*)	1 S	1 S	200 S	1 F
Co	3 S— (*u*)	200 S	1 S	1 S	1 S
Ca	..	..	..	200 S	..
Ba	..	..	..	2 S	..

Notes to Tables.

(*a*) The presence of aluminium in the reagents made the result doubtful.

(*b*) A distinct precipitate of $Al(OH)_3$ was obtained in P. 53, but not more than with the reagents alone.

(*c*) Excess of HCl was added in P. 53 and the solution boiled, as a result of which the chromic acid was reduced. On analysing another mixture, and using HNO_3, a satisfactory test for chromium was obtained.

(*d*) The absence of manganese was confirmed by fusing some of the iron salt on platinum foil with Na_2CO_3 and KNO_3; no green colour was obtained.

(*e*) A small precipitate of ZnS was obtained in P. 57, which did not contain more than 1 mgrm. Zn. See C. E., P. 52, N. 11.

(*f*) A small precipitate of ZnS was obtained in P. 57, corresponding to 2 or 3 mgrms. Zn.

(*g*) In this analysis a large excess of alkali was added before the Na_2O_2 in P. 52, and the mixture was well stirred.

(*h*) This analysis was repeated except that the acid solution in P. 42 was poured slowly into an excess of hot alkali before adding Na_2O_2; a distinct test for zinc was then obtained in P. 57.

(*i*) A distinct test for calcium was obtained (except possibly in T. A., No. 148); the iron salt was found to contain about 2 mgrms. Ca with 500 mgrms. Fe.

(*k*) This analysis was repeated except that no Na_2CO_3 was added in P. 52; the test for chromium failed.

(*l*) See C. E., *P 58*b*, N. 2.

(*m*) The precipitate of $Be(OH)_2$ obtained in *P. 58*h* was large, and corresponded to 2 mgrms. Be, thus showing that much smaller amounts could be easily detected.

(*n*) The basic acetate procedure (P. 65) was used instead of P. 64; good tests for thallium were obtained both in the precipitate and in the filtrate. (Compare C. E., P. 65, N. 6).

(*o*) Chromium was lost in *P. 58*a*, owing to the presence of H_2O_2 (from the peruranate, see C. E., P. 52, N. 6, and *P. 58*b*, N. 2), and the addition of a large excess of acid.

(*p*) A slight blue coloration was obtained with H_2O_2 in *P. 58*b*, corresponding to not more than 0·5 mgrm. Cr. No lead nitrate was added.

(*q*) The directions in *P. 58*c* were faulty; too little phosphate was added to precipitate 1 mgrm. U.

(*r*) A good test for aluminium was obtained in *P. 58*g*, but the confirmatory test (P. 54) failed.

(*s*) The test for iron in P. 65 was a failure; the iron was found with the manganese in P. 62.

(*t*) Satisfactory tests for iron were obtained in P. 62 and in P. 64.

(*u*) $(NH_4)_2S$ was used instead of H_2S in precipitating the sulphides in P. 66, and some nickel was lost in the brown solution. Nickel and cobalt were also lost in P. 67 in the treatment with dilute HCl, owing to the rejection of the Na_2O_2 precipitate.

(*x*) Only a few mgrms. of vanadium were found in the filtrate from P. 51.

(*y*) About twice as much zinc was found in P. 57 as in P. 67.

(*z*) Owing to the insolubility of $Zr(OH)PO_4$ it is scarcely possible for zirconium and phosphate to occur together in the analysis of the aluminium and iron groups. The zirconium was undoubtedly lost in dissolving the precipitates obtained in P. 52—65.

for the analysis of mixtures containing only the common elements was at that time substantially the same as given above. In these tables the numbers in each vertical column show the weights in mgrms. of the various elements which the solution submitted to analysis contained. The results of the tests for each element are shown by the letters following these numbers. That the result was satisfactory is indicated by the letter S; that is, when the element was present, that the test for it, however small, was unmistakable, and therefore conclusive; and when the

element was absent, that a good blank test was obtained. When the test was very small, especially in comparison to the quantity of the element present, though still unmistakable, this is sometimes indicated by the symbol S—. When in the presence of the element the test failed, or in its absence a result was obtained that might be thought to indicate its presence, the letter F is used. When the result was doubtful or inconclusive, owing to the appearance or small size of the precipitate, this is indicated by the letter D. When the test was not tried, if the element was present a dash is used in place of a letter; or, if the element was not present, dots are inserted.

Common Elements.

Analyses Nos. 114—119 were begun at P. 51; P. 61 was introduced before P. 52.

Analyses 120—125 were begun at P. 61.

Analyses 125—127 were made by P. 69; analyses 128—130 by P. 70.

Analyses Nos. 131—143 were begun at P. 52.

Analyses Nos. 114—155 were begun at P. 52; P. 61 was omitted.

Mixtures containing the Rarer Elements.

Analyses 156—161 were begun at *P. 58*a*.

Analyses 162—165 were begun at *P. 58*f*.

Analyses 166—170 were begun at *P. 58*a*.

Analyses 171—176 were begun at P. 64; analysis 176 at P. 52.

Analyses 177—181 were made by Mr. R. D. Gale, who had had no previous experience in connection with the process. The first analysis was with a known mixture, the remaining four were with unknowns. Mr. Gale received no assistance while making an analysis (except in T. A., No. 179), but all the precipitates and solutions were preserved in order that the causes of mistakes might afterwards be investigated. The process was practically in its final form with exception of the procedures relating to the separation of chromium, uranium, and vanadium (*P. 58*b*—*e*), which were revised on account of the results of these analyses; moreover, uranium was not tested for in *P. 58*h*. Test analyses 156—161 and 166—170 were made at a later date to test these procedures in their final form.

Although all possible combinations of small and large quantities of the elements have not been investigated, the test analyses are sufficiently varied to justify general conclusions as to the reliability of the method of separation and detection of the elements.

An examination of these analyses shows that 1 mgrm. of any of the seven common elements in various combinations with one another and in the presence of the rarer elements was detected in almost all cases, even when the element was associated with a large quantity of other elements. Zinc frequently escaped detection in the analysis of the aluminium group (in P. 57), but was then always found in the analysis of the iron group (in P. 67) when tested for (see T. A. 131—153, 178, 180). One mgrm. is, however, near the limit of detectability when the elements of the iron group are present in large quantity. Two mgrms. of chromium were lost in two cases (T. A. 118, 181) owing to the reduction of the chromate; these analyses served to emphasise the necessity of added precautions, which have since been provided for in the directions. One mgrm. of iron in the presence of a large quantity of manganese would have been overlooked (in T. A. 180) if it had not been tested for in the solution of the chloric acid precipitate, as directed in P. 62. In the case of aluminium, owing to its being contained in the reagent, it was sometimes difficult (see T. A. 116, 117, 119, 131—136, 144—149) to determine with certainty whether or not 1 mgrm. was present.

It will be seen from T. A. 142—151 and 180 that the presence of much phosphate does not interfere with the detection of 1 mgrm. of any of the common elements of these groups. It does, however, cause a larger quantity of zinc to be completely precipitated by sodium peroxide (compare T. A. 141 with 142 and 143). It is shown by 144—146, 150, 151, and 180 that 2 mgrms. of barium and 1 mgrm. of magnesium are detected in the process, showing that adequate provision is made for the recovery of the alkaline earth elements when carried down with these groups, through the presence of phosphate.

The analyses with the rarer elements (T. A. 156 to 181) show that the process led to the detection of 1 mgrm. of each of these, and even of 0·5 mgrm. of beryllium and titanium in all cases except the following:—In T. A 180 zirconium was missed, owing to the simultaneous presence of much phosphate; but, even in the absence of phosphate, 1 mgrm. is not far from the limit of detectability in a complete analysis. In T. A. 166, 168, 170, and 178 uranium was missed in the usual place (in *P. 58*c* and *d*) owing to the fact that it was carried down with aluminium or beryllium in the treatment with dilute $NaHCO_3$ (*P. 58*a*), but T. A. 168 and 170 and a number of special experiments with mixtures of beryllium and uranium show that in such cases uranium can be detected in *P. 58*h*.

(To be continued).

IMPRESSIONS OF THE FIRST INTERNATIONAL FOOD CONGRESS.

By LOUDON M. DOUGLAS,
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The first Congress of an international character, which has just been held at Geneva, will be memorable because of the widespread interest it evoked. The idea of such a Congress has often been in the minds of those associated with food supply, but the standards vary so much in different countries that at the outset it may be admitted that the difficulty of meeting upon some common ground has so far prevented international action. The value, also, of any resolutions passed must, for the greater part, be of an entirely academic character, inasmuch as it is clear that indiscriminate voting at such a Congress on any specific resolution must be unequal, and the nation with the preponderance of representatives present must control the issues.

To be of any value, therefore, such Congresses must appoint an equal number of delegates who have power to vote, and it might be arranged to protect the interest of minorities by giving them power to co-opt representatives from other nations, so as to equalise their voting power.

The Congress, which was held at Geneva from September 8th to 12th inclusive, under the auspices of the Society of the White Cross of Geneva, owes its origin to Frenchmen, and Mr. Ruau, the French Minister of Agriculture, attended its deliberations, and also outlined his own and presumably his Government's attitude in relation to the food supply. The fact that out of the 400 odd delegates present from all countries some 250 were French, serves to illustrate the point that voting upon any resolution under such conditions could not be described in any sense of the word as representative of international opinion.

The primary object which the Society hopes to attain is described in the title, which states that it exists for the Repression of Frauds in Food and Pharmaceutical preparations. With such a *rôle* it will be admitted that it has a vast field of activity before it, but the political element must be suppressed, otherwise it is quite clear that such a society may be made simply the tool of whichever country cares to exploit it the most.

There were twenty-nine different nations represented, but some of these had only a very limited number of delegates present, and many were quite unofficial, having come on their own initiative. This was noticeable with

regard to the United Kingdom, which was not officially represented, although the Local Government Board had intimated that such a delegation would be sent.

The programme presented to the Congress was a large one, and dealt with many subjects in varying aspects, the discussions being largely made up of a mixture of science and commerce. The first day's proceedings were taken up with arriving at a definition of wine, but from the British point of view that is a subject which has only a local interest. The definition arrived at, however, may be of interest outside of wine-growing countries. Wine was defined as being generally the product of the alcoholic fermentation, complete or incomplete, of fresh grapes or of the juice of fresh grapes. The signification of the definition lies in the fact that during recent years much sophistication has taken place in wines, more especially for export; with the consequence that the demand has gone down considerably, and over-production has caused much depression in the wine districts of both France and Spain.

Vinegar was also defined as the exclusive product of the acetic fermentation of wine, but that is clearly a definition suited to France or Spain and few other countries. Other definitions of an equally comprehensive character were given for cider, perry, beer, and liqueurs.

The second day was devoted to defining milk, butter, cheese, eggs, fats used for foods, and various commodities associated with "charcuterie," which is in reality the business of pork purveying and the manufacture of pork products. With it, however, is associated preserved and other provisions.

The definition of butter proved to be the one in which most interest was taken, and the discussions regarding what pure butter really was sometimes became very animated indeed. Finally, however, it was agreed that butter was a mixture of fatty matters exclusively derived from cow's milk after fermentation, and made either from whole milk, separated fat, or a mixture of both.

The use of preservatives in butter naturally occupied much attention, and while many of the French delegates opposed it, others as effectively supported it, and it was soon apparent that a large number, inclusive of the British delegation, were strongly in favour of a definition that boric acid preservatives should certainly be allowed. Such opposition as exhibited itself seemed to be from a section which did not attempt to specify any objection from the point of view of health, but rather from the point of view that the use of preservatives favoured the manufacture, as distinguished from the farmer or the co-operative societies. No decision, however, was reached, and the whole question was postponed to a further conference, to be discussed under the head of "Manipulation."

The British section, through their spokesman Dr. Tunnicliffe, pointed out that the descriptive text in which the attitude of the various nations to this matter was given, was entirely wrong in stating that the use of preservative in the United Kingdom was prohibited, and that, on the contrary, it was allowed by the responsible Department of State up to 0·50 per cent. A further discrepancy in this definition also appeared in the absence of any reference to the allowable percentage of water. On the whole, the matter was left in a very unsatisfactory condition, and it may be assumed that at the next Congress the necessity for boric acid as a preservative, in addition to salt, will not only be recognised as desirable, but will be declared to be essential in all butters which have to be kept for any length of time beyond two days.

Cheese was defined as being the product of whole milk treated in the usual manner, but, of course, such a definition can have no weight whatever. The milk from which cheese is made varies considerably, as does also the recognised fat contents of cheese, and it will need much greater precision in definition before a clear understanding can be arrived at. Eggs, again, were only entitled to be described as fresh when not submitted to any process of preserving, and oils and other fats did not attain any more definite descriptions. Frozen meat was placed in the category of preserved meats!—a definition which will hardly be accorded general approbation—and sausages were only entitled to be described as "pure" when free from all other ingredients except meat, pork, or veal, in addition to the seasonings! They ought not to contain any greater percentage of moisture than the natural moisture of the ingredients. Of the other articles in the same class, none call for any special notice except salted meats, which were defined as being made from meats salted exclusively with commercial salt, with the addition of variable quantities of saltpetre and sugar. The inclusion of such a preservative as saltpetre may be regarded as indicating that the principle of using other preserving agents besides salt is unavoidable, and in this connection the general opinion was that it will be found impossible to inhibit the production of certain ptomaines without the use of boric acid or other similar preservative.

The manufacturers of cocoa seem to be very much divided as to what that article really is, as, judging from the discussion, the partisans of the use of alkaline carbonates maintained successfully that the addition of such chemical products did not interfere with the purity of the substance. The question is one for manufacturers, and some of these whose names are known in many countries insisted on the recognition of this principle.

As with cocoa and its cognate productions, so with tea and coffee. Purity from admixtures of all kinds was the keynote throughout.

In the departments of mineral waters, pharmaceutical preparations, and the unification of analytical methods, it would seem to be rather difficult to obtain such definitions as would be acceptable to all countries, as the practice must necessarily be governed by local tradition to a great extent, as well as the demands of the public. It is desirable from the International point of view that there should be unification of formulæ, but such a result can hardly be expected from a mixed Congress such as this, and, indeed would seem to be altogether out of its province.

On the whole, the first International Food Congress may be said to have been interesting as an opportunity for the exchange of opinions on many questions affecting the food supply, and the very inconclusiveness of the discussions would seem to demonstrate the necessity for better organisation in the future. The Congress may be looked upon as being established, and is likely to continue from year to year. Possibly it may be found practicable to invite the various national representatives to the United Kingdom, so that the British nation may also have an opportunity of witnessing in detail what precautions are considered necessary in the handling of food in other countries. It must always be remembered that we are more interested than other nations in this aspect of the question, as we are buyers of food supplies to a greater extent than any other.

It only remains to be said that the thanks of the Congress are due to the secretary, M. Fazy, and the Local Committee, for the excellent arrangements made. Thanks are also due to the University of Geneva for placing the rooms and hall of their classic institution at the disposal of the Congress. The ticket of membership carried the delegates to the Kursaal, and a fête at the Parc Eaux-vives arranged by the Committee of the Society of the White Cross of Geneva, and many other well-appointed functions.

As showing also the interest taken in the work of the Society, it may be mentioned that a princely donation of 100,000 francs was given by Madame Paul Bolo, and many others of a lesser amount have also been received. In so far as the British section is concerned, arrangements will be made in the future for a proper organisation, and permanent secretaries will be appointed to represent the manufacturers and the scientific sections of the United Kingdom, so that the next Congress, which will be held in Paris next year, will be attended by a British delegation worthy of the subject.

NOTICES OF BOOKS.

General Inorganic Chemistry. By ALEXANDER SMITH, B.Sc. (Edin.)., Ph.D. (Munich), F.R.S.E. London: George Bell and Sons. 1907.

A LOGICALLY presented treatment of inorganic chemistry is to be found in this book, which is suitable for the use of college students beginning the subject, or possibly for the pupils in the highest classes of schools. It is not by any means easy reading, and makes considerable demands upon the powers of concentration, but no parts are really beyond the comprehension of the well-prepared student. In one respect it differs from other books of the same scope, namely, the treatment of the theoretical side of the subject. Although there is, perhaps, not more theory than it is generally thought to be advisable to put before the first year student, the discussions of it are made much more prominent and detailed than usual, and descriptive and historical chemistry are treated only as illustrating the general theoretical principles of the science. The author thinks that the consultation of reference books for additional descriptive matter offers no difficulty to the ordinary student, while it is otherwise with theory, and there seems some justification for his idea that the books at the student's disposal should include one treating theory fully and a reference book of purely descriptive chemistry instead of one for general use, treating description fully, and a theoretical reference work. The book contains some exercises, largely on calculations, and the order in which the different subjects are introduced seems thoroughly satisfactory.

La Canfora Italiana. ("Italian Camphor"). By ITALO GIGLIOLI. Rome: Giovanni Bertero and Co. 1908.

THIS monograph is a reprint with considerable additions of reports which were presented to the Sixth International Congress of Applied Chemistry held in Rome in 1906. It gives an account of the history, commercial value, cultivation, and geographical distribution of *Laurus Camphora*, and special attention is paid to the possibilities of growing it successfully in Italy. Modern analytical researches on camphor and oil of camphor are described, and their extraction from the leaves of *Laurus Camphora* is fully treated. The bibliography of the subject is particularly carefully compiled, and includes books in all languages, and the references in the text to original papers are very full. A few notes are added on the preparation of celluloid with Italian camphor.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xli., No. 11, 1908.

Titanium Nitride and a New Class of Titanium Compounds.—Otto Ruff and Fritz Eisner.—The titanium nitride to which Wöhler, Friedel, and Guérin ascribed the formula Ti_3N_4, and Schneider's "Nitride A," consist of the nitride of trivalent titanium, TiN, containing titanium nitrogen chloride and titanium dioxide as impurities, and when it is heated for some time to a high temperature in a current of ammonia, the chlorine and oxygen are completely removed and the pure nitride, TiN, is left behind. When liquid ammonia is added to titanium tetrachloride or tetrabromide and the product is washed with liquid ammonia, compounds are formed which contain at least one atom of halogen, or the corresponding amount of oxygen to one atom of titanium. They are transformed into the titanium nitrogen haloids, TiNCl and TiNBr, on heating, and on being more strongly heated they yield titanium nitride, titanium tetrachloride, or bromide and nitrogen. They are exceedingly sensitive towards moisture. The fact that the halogen is more strongly bound to titanium than to silicon (the tetrachloride of which is completely decomposed by ammonia) shows the more strongly positive character of titanium. It is noteworthy that titanium readily passes from the tetra to the trivalent state at a high temperature if it is combined with the less negative nitrogen instead of with chlorine or bromine.

Catalytic Reductions with Colloidal Palladium and Platinum.—C. Paal and Josef Gerum.—The authors have extended their experiments on the action of colloidal palladium and platinum to the unsaturated acids and their derivatives; *e.g.*, fumaric, maleic, and cinnamic acids, and cinnamic acid methyl ester. They have found that the acids are readily reduced by colloidal palladium to the saturated acid succinic acid. Colloidal platinum has a much feebler catalytic action, as shown by the much smaller velocity of the reaction.

Catalytic Reductions with Colloidal Palladium.—C. Paal and Karl Roth.—Oleic acid is reduced by colloidal palladium at the ordinary temperature, giving a good yield of stearic acid. Colloidal palladium reacts readily with castor oil, which is completely hydrated; with olive oil the hydration is not nearly so complete, though it takes place to a certain extent. Cod-liver oil under similar conditions is completely hydrated.

Lecture Experiments to Prepare Hydrocarbons.—James Frederick Spencer.—To prepare pentane (or isopentane) 2 to 3 grms. of amyl (or isoamyl) iodide are heated with the theoretical amount of dry magnesium until the reaction begins, when the heating is stopped. When the reaction is over the product is cooled, and water is added drop by drop, when pentane is evolved. Benzene can be prepared by the same reaction, benzyl iodide being substituted for amyl iodide. Similarly, α-bromnaphthalene yields naphthalene.

Coloured and Colourless Triphenylmethyl.—Julius Schmidlin.—The colourless crystals of triphenylmethyl dissolve to a clear colourless liquid in benzene, chloroform, and other solvents. The liquid turns yellow after a few seconds, but the colour disappears on shaking. The liquid again becomes coloured on standing, and loses its colour on shaking, and this process of coloration and decoloration can be repeated until finally the decolorised solution remains colourless on standing. This phenomenon is characteristic of all triphenylmethyl preparations, and apparently in the coloured solutions two chemical individuals exist, one colourless and the other coloured. Each form can be changed into the other, and in the solid and also in the dissolved state the two forms are in a definite state of equilibrium, which is dependent on the solvent and the temperature. The colourless triphenylmethyl is less soluble than the coloured variety, for triphenylmethyl separates from the yellow solution in colourless crystals.

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THE CHEMICAL NEWS.

Vol. XCVIII., No. 2551.

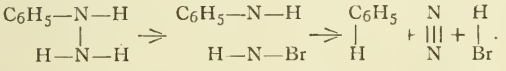
THE ACTION OF HALOGENS UPON AROMATIC HYDRAZINES.*

By F. D. CHATTAWAY, D.Sc., F.R.S.

The actions which take place when the halogens are brought into contact with primary aromatic hydrazines are so violent, unless special precautions are taken, and such large amounts of tarry matters are formed, that they have been investigated comparatively little, and in consequence the formation of the many different substances which are produced when the conditions of interaction are altered has never been accounted for satisfactorily.

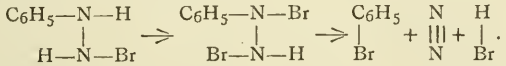
The complicated changes which occur all depend, however, upon a progressive substitution of hydrogen attached to the nitrogen, followed by a breaking down of intramolecular rearrangement of the N-substituted hydrazines thereby produced.

When a halogen acts upon an aromatic hydrazine one of the hydrogen atoms of the —NH—NH_2 group, probably one in the —NH_2 group is replaced,† a nitrogen halogen derivative being produced which at once undergoes what is in fact the typical diazo decomposition—for example :—

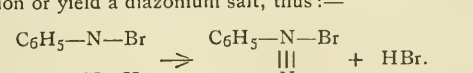


Hydroxyl ions much accelerate the rate at which this decomposition occurs, while hydrogen ions correspondingly diminish it.

When halogens therefore act upon aromatic hydrazines in presence of alkalis, hydrocarbons, the hydrides of the aromatic groups present in the hydrazines, are almost exclusively produced. When, however, an excess of halogen is employed a relatively small amount of the N-monosubstituted hydrazine undergoes further substitution before disruption can take place and a dihalogen N-substitution product is formed, which, like the monosubstitution product, is unstable in presence of alkali and breaks down similarly, a monosubstituted halogen derivative of the hydrocarbon formed in the first action being produced—for example :—

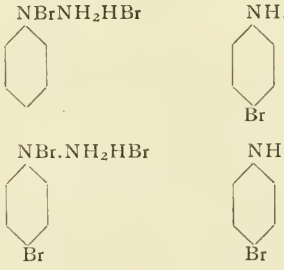


The N-monosubstituted hydrazines being far more stable in presence of acids, when these are present this replacement of a second halogen atom takes place to a much greater extent, and the whole of the hydrazine may thus be converted into the N-substituted derivative, which then may, according to conditions, undergo the diazo decomposition or yield a diazonium salt, thus :—



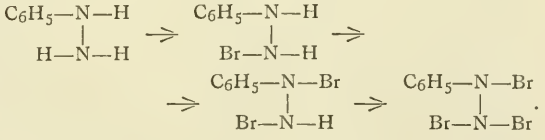
The diazonium salt may, if suitable means are adopted, be isolated (Chattaway, *Trans. Chem. Soc.*, 1908, xcviii., 852), but as the interaction of halogen and hydrazine is usually very vigorous and accompanied by considerable evolution of heat, it is generally decomposed, giving rise to tarry matters.

In presence of a considerable excess of hydrochloric or other strong acid the NH_2 group is to a large extent protected* against the action of the halogen and substitution takes place most readily in the —NH— group. The nitrogen halogen compound thus produced is of the type of the acyl amino compounds, and under the influence of the acid undergoes the intramolecular rearrangement characteristic of these compounds, whereby the halogen passes into the para or ortho position in the nucleus. Mono and disubstituted hydrazines are thus produced—for example :—

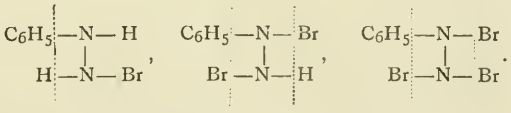


Further substitution into the remaining ortho position has not been observed, and probably cannot be effected, since the substitution of halogen so lessens the basicity of the hydrazine that the NH_2 group is attacked by preference ; indeed the yield of mono or disubstituted hydrazine is never satisfactory, diazonium salts and their decomposition products always being produced in large quantity.

The author has recently shown (*Proc. Chem. Soc.*, 1908, xxiv., 172) that when the required amounts of bromine are added to aromatic hydrazines dissolved in acetic acid, diazonium perbromides, which are thus N-tribromosubstituted hydrazines, are produced quantitatively. The replacement of hydrogen in the —NH.NH_2 group can thus be carried to completion—for example :—



Each of these substitution products can undergo the typical diazo decomposition quantitatively when the conditions are favourable. Thus by the action of bromine upon phenylhydrazine we can obtain either benzene or bromobenzene, nitrogen and hydrogen bromide or bromine being eliminated thus :—



Other compounds besides these simple ones may be formed—for example, from among the products of the action of bromine on phenylhydrazine, in addition to benzene and bromobenzene, *p*- and *m*-dibromobenzene and 1, 2, 4 and 1, 3, 5 tribromobenzene have been isolated, as well as azobenzene and diphenyl ; the formation of all these products can be simply explained by the theory of the reaction here put forward. It is, moreover, entirely in harmony with all that has been observed in the oxidation of the aromatic hydrazines.

* A Paper read before the British Association (Section B), Dublin Meeting, 1908.

† This, as in other similar cases, is without doubt effected by the addition of two atoms of the halogen, followed by the elimination of a molecule of halogen hydride.

* This is probably due to the addition of halogen necessary for substitution to take place being prevented by the combination of the NH_2 group with the acid.

THE RATE OF PRODUCTION OF HELIUM FROM RADIUM.

By Sir JAMES DEWAR, M.A., Sc.D., LL.D., F.R.S.

Some time ago I communicated a paper to the Society entitled "Note on the Use of the Radiometer in Observing Small Gas Pressures: Application to the Detection of the Gaseous Products produced by Radio-active Bodies" (*Roy. Soc. Proc.*, 1907, A, lxxix., 529). In the course of the experiments recorded in that paper it was shown that a pressure of the fifty millionth of an atmosphere could easily be detected by radiometer motion, and that the helium produced by radio-active processes from some 10 mgrms. of bromide of radium could be definitely detected after a few hours. This led me to desire some direct measurements of the amount of helium produced by radium, and through the kindness of the Royal Society in allowing me the use of some radium chloride belonging to them I am able to give a condensed abstract of the experimental results so far obtained.

The salt employed was the 70 mgrms. of radium chloride prepared by Dr. T. E. Thorpe, F.R.S., for his determination of the atomic weight of radium, the preparation of which is fully described in *Roy. Soc. Proc.*, A, lxxx., 298.

The apparatus used for the measurements was a McLeod gauge in the construction of which no indiarubber joints were used; the mercury reservoir being connected to an exhaust pump, while the elevation and lowering of the mercury was carried out by admitting and exhausting air in the reservoir. The air coming in contact with the mercury was purified by passage over stick-potash and phosphoric anhydride. Sealed on to the gauge was a long U-tube containing a ¼ grm. of cocoanut charcoal placed in a small enlargement at the bend, the whole being arranged for liquid air or other cooling for any desired length of time. The object of the use of this cooled charcoal is to take up and condense all adventitious gases, other than hydrogen or helium, which might arise from minute leakage or otherwise be generated in the apparatus. The radium chloride was contained in a small bottle standing in a cylindrical glass bulb connected by a T-joint to the U-tube. To the other arm of the T was sealed a bulb containing about 15 grms. of cocoanut charcoal for producing a high exhaustion in the apparatus when cooled to −190° C. The whole apparatus was well exhausted by mechanical means, all the glass tubes being heated as well as the charcoal receptacles and the radium chloride. On immersing the receptacle containing the 15 grms. charcoal in liquid air for some hours, while the ¼ grm. charcoal and the radium chloride were kept hot, an exhaust of 0·00015 mm. was obtained. This charcoal receptacle was now sealed off, and the small ¼ grm. charcoal tube cooled in liquid air. In two hours an exhaust of 0·000054 mm. was reached.

The volume of the gauge and apparatus being approximately 200 cc., a knowledge of the pressure in the apparatus gives by a simple calculation the actual volume of gas produced measured at atmospheric pressure and the temperature of the laboratory, and thus the rate of production of helium is obtained. This, referred to the weight of radium present, gives the increment in terms of cubic millimetres of gas per grm. of radium per day.

During the first three days the growth of pressure was very small, amounting to about 0·3 cub. mm. per grm. of radium per day. This was, however, practically all produced in the first day. On then heating the radium the pressure was increased to an amount corresponding to an increment of 0·99 cub. mm. The laboratory having to be closed for a fortnight no observations were taken, and as no part of the apparatus was cooled the emanation had free play throughout. About the 350th hour after heating the radium salt the pressure had increased to a value exactly corresponding to the 0·99 cub. mm. increment observed after the first three days. This rate was, however, only kept up for the two succeeding days during which the radium was not heated. On heating the radium a further increase of pressure was obtained (corresponding to a 1·1 cub. mm. increment measured from the start), which largely disappeared on cooling the radium, and did not reappear on presently heating the radium again. From this stage throughout the next 120 hours the pressure rapidly became less, despite the heating of the radium, which only temporarily and partially restored it; and after 610 hours a lower pressure was recorded than that obtained immediately after the period of no observations, *i.e.*, after 400 hours.

The charcoal was now heated to 450° C. by boiling sulphur. Then on again cooling it with liquid air the pressure was found to have been restored by an amount equal to one-third of that lost as stated above. This, however, quickly disappeared, and apart from fluctuations caused by heating, the radium remained during the next 300 hours at about the value observed just before heating the charcoal to 450° C.

At this point the charcoal was again heated in boiling sulphur, and the previous result was repeated. In the ensuing 150 hours, however, the pressure, after falling a little, remained fairly steady, and then showed a definite and maintained increase for three days, not permanently affected by again heating the charcoal to 450° C.

The quantity of permanent gas produced up to 1100 hours corresponded to an increment of 0·417 cub. mm. per grm. of radium per day taken over the whole period. At this point the radium was sealed off, and the first experiment ended.

The large increase over the period in which the charcoal and the radium were both at ordinary temperatures may find some explanation from the unchecked action of the emanation on the charcoal, organic matter, and combined moisture possibly present on the walls of the glass tubes of the apparatus, in quantities though small yet large enough to produce the total amount of gas present which, as measured with charcoal at the ordinary temperature, corresponded to a pressure of 1 to 2 mm.

It may be noted that on the supposition of this gas being largely due to a continuous air leak, the amount of uncondensed gases of the helium type thus introduced would be infinitesimal.

Apart from the possible presence in the apparatus of organic material the radium itself might conceivably at the beginning have been contaminated with traces of organic matter, and a further experiment was decided on to which these objections could not be applied.

In the second experiment the gauge as well as the connecting tubes were well cleaned out with nitric acid, and all thoroughly dried. The radium, after the 1100 hours in which it was under high exhaustion and had been frequently heated, was certainly in a more satisfactory condition. Further, to prevent the unchecked action of the emanation throughout the apparatus, the little charcoal condenser was maintained at a degree or two below that of the boiling-point of oxygen by the use of old liquid air for a period of about six weeks. A larger quantity of charcoal was used, viz., 1 grm., the more effectively to condense out extraneous gases while leaving any helium substantially unaffected. This charcoal had been treated with chlorine at a red heat and subsequently with hydrogen.

Beyond this the conduct of the experiment followed the lines of the former one. The mercury pump exhaust was continued for several hours, and was carried to 0·002 mm. The large charcoal bulb was then cooled for several hours in liquid air while heating the 1 grm. of charcoal and the radium salt. A pressure as low as 0·00005 mm. was thus obtained when the charcoal was sealed off. On now placing the U-tube containing a small quantity of charcoal in liquid air the pressure registered was 0·000044 mm.

These conditions were maintained for five days, during which a steady growth of pressure was observed corresponding to an increment of approximately 0·3 cub. mm. per grm. of radium per day. The radium was then heated with a small Bunsen flame as before to a low red heat, when the pressure was increased by about 40 per cent. This increase showed no sign of disappearing, but during

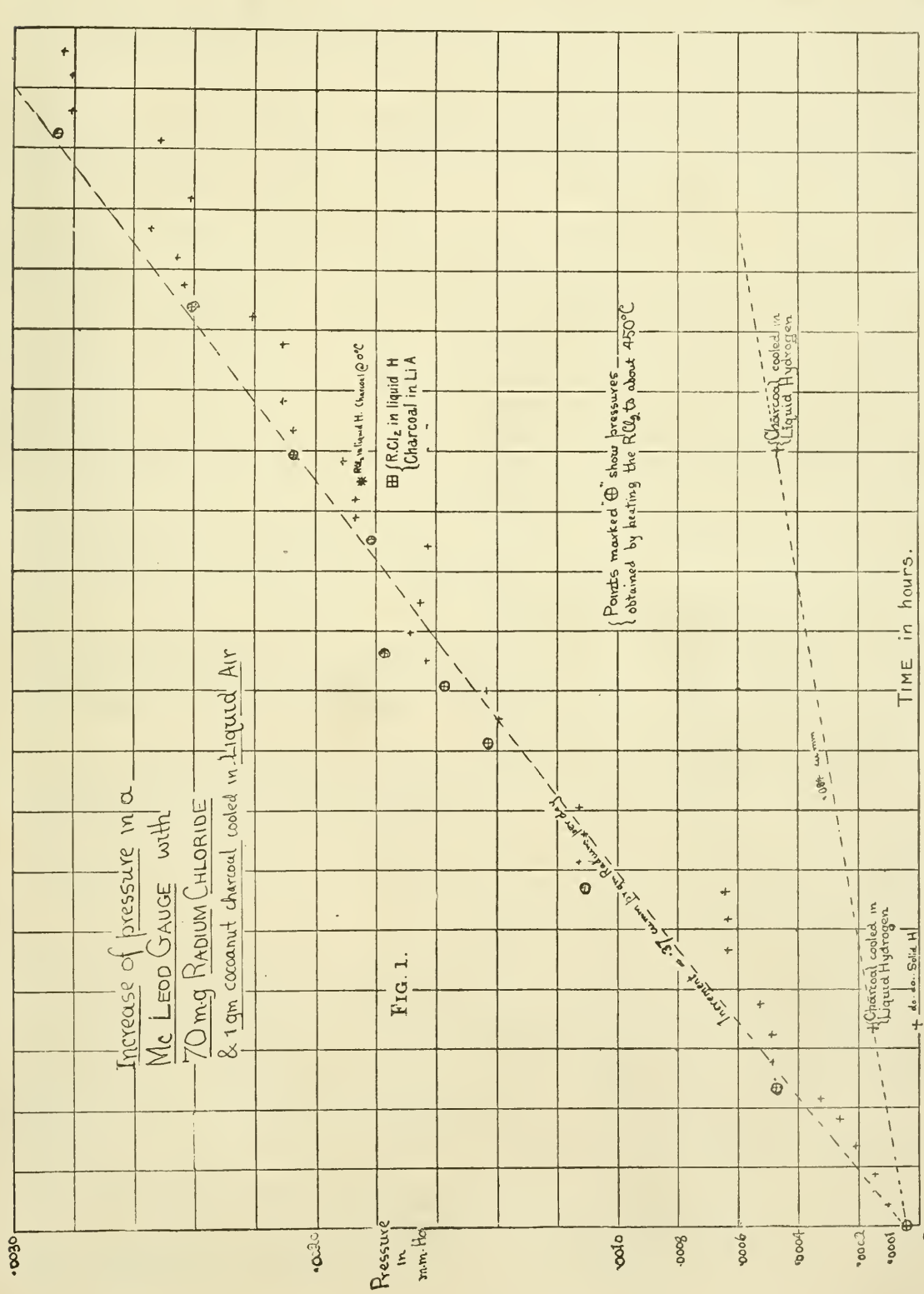

Increase of pressure in a
Mc LEOD GAUGE with
70 m.g RADIUM CHLORIDE
& 1 gm cocoanut charcoal cooled in Liquid Air
⊞ (R.Cl₂ in liquid H
(Charcoal in Li A
* RCl₂ in liquid H. Charcoal @ 0°C
{ Points marked ⊕ show pressures
{ obtained by heating the RCl₂ to about 450°C
+ Charcoal cooled in Liquid Hydrogen
+ Charcoal cooled in Liquid Hydrogen
+ do. do. Solid H
Pressure in m.m. Hg
TIME in hours.
0
50
100
200
300
400
500
600
700
800
900
1000
.0030
.0020
.0010
.0008
.0006
.0004
.0002
.0001

FIG. 1.

the next week a decided but somewhat irregular growth of pressure was recorded. The radium was again heated, when a further increase of pressure was observed. In the succeeding five days it remained steady, only to be again increased on heating the radium. This treatment was repeated in all ten times at varying intervals during 1100 hours, and in each case the pressure rose on heating, and remained fairly steady on standing. All the observations of the second set of experiments are graphically represented in Fig. 1. A mean line is drawn through the observations taken with the radium heated, giving a steadily maintained helium increment of approximately 0·37 of a cub. mm. per grm. of radium per day.

In order to ascertain if any helium was occluded in the cooled charcoal and the surrounding glass, the latter was raised to a low red heat, while the tube containing the radium chloride was temporarily cooled in liquid air, with the object of condensing out and localising the emanation coming from the heated charcoal and preventing its access to the gauge. The temperature was maintained for an hour, and then the charcoal was allowed to cool and finally replaced in the liquid air. The radium chloride was then allowed to warm up, and was heated to near a low red for a short time. After these alterations no increase in pressure was observed, from which it may be inferred that the occlusion of the helium takes place mainly in that part of the apparatus where the radium chloride is situated.

On two occasions the charcoal was cooled in liquid hydrogen, viz., after 165 hours, and again after 650 hours. The proportionate reduction of pressure was the same in both cases, tending to show that the composition or nature of the gas remaining uncondensed by the liquid air remained the same throughout, although steadily increasing in quantity.

In reference to this last point a separate experiment was made in which pure helium under a small tension, produced by heating 0·5 grm. uranite and passing the gas produced over 1 grm. charcoal cooled in liquid air, was subjected to the action of ¼ grm. of clean exhausted charcoal at the temperature of liquid air and liquid hydrogen respectively. The ratio of the two pressures so obtained was in close agreement with that observed in the radium experiment.

A further test of the purity of the gas producing the permanent pressure observed in the radium experiment with the charcoal cooled in liquid air was made by simply cooling the bulb containing the radium in liquid hydrogen, allowing the charcoal meanwhile to warm up to 0° C. If any hydrogen was present in the gas it is certain that there would be an increase of pressure recorded, since although hydrogen is partially absorbed by charcoal in liquid air, yet it would not be reduced in pressure by cooling in liquid hydrogen. On allowing the charcoal therefore to warm up, any hydrogen expelled would remain and cause an increased pressure. Inasmuch as an increase was not recorded, it can be safely assumed that no hydrogen is present, and thus the gas pressure measured consists entirely of helium.

A confirmation of this was made spectroscopically as follows:—Two tin-foil electrodes were placed round the narrow capillary measuring tube of the gauge, near the closed end. These were about 3 cm. long and about 1½ cm. apart, and were wired on with thin copper wire. The gas was compressed into this capillary space, as in taking an ordinary measure to any pressure of the order of 2 or 3 mm., while an induction discharge passed in the gas. The spectroscopic examination of this discharge revealed only the six principal helium lines, mercury, and a trace of the carbonic oxide spectrum. I have shown that the carbonic oxide spectrum always occurs in electrodeless tubes (see paper, *Roy. Soc. Proc.*, lxiv., 237, "On the Application of Liquid Hydrogen to the Production of High Vacua, together with their Spectroscopic Examination").

I am not aware of any previous direct measurements of the rate of production of helium from radium, but in a paper on "Some Properties of Radium Emanation," by A. J. Cameron and Sir William Ramsay (*Journ. Chem. Soc.*, 1907, p. 1274), the ratio of the amount of helium produced to that of the emanation was found to be 3·18, and as the amount of the emanation found by them was about 1 cub. mm. per grm. of radium per day, the resulting helium according to this experiment ought to reach about 3 cub. mm., or at least eight times the rate of production found in the above experiments. I am at a loss to explain the origin of such grave discrepancies in the measured amount of the helium produced by radium. (Prof. Rutherford, in a paper, "Experiments with Radium Emanation," *Phil. Mag.*, July, 1908, shows this result is at least ten times too great, his value being of the order 0·11 cub. mm. of emanation per day, whereas from my experiments the rate of helium production is just three times this amount). On the other hand, Prof. Rutherford, in his work entitled "Radio-active Transformations," 1906, p. 186, on the theoretical assumption that the α-particle is an atom of helium carrying twice the ionic charge, deduced from electrical measurements that the number of particles expelled per year per grm. of radium would reach 4×10^{18}, and as 1 cc. of a gas at standard temperature and pressure contains $3{\cdot}6 \times 10^{19}$ molecules, the volume of helium produced per year would amount to 0·11 cc., which is equivalent to about 0·3 of a cub. mm. per day. Considering I have found a rate of helium production of the order of 0·37 cub. mm., the agreement between experiment and the theoretical prophecy of Rutherford is almost too wonderful, substantiating as it does the accuracy of the theory of radio-active changes he has done so much to initiate and develop.

I have to express my obligations to Mr. Robert Lennox, F.C.S., and Mr. W. J. Green, B.Sc., for aid given in the conduct of these long and laborious experiments.—*Proceedings of the Royal Society*, 1908, A, lxxxi., 280.

THE FRUIT OF THE *CAULOPHYLLUM THALICTROIDES* AND *CORNUS SERICEA*.

By EDITH STOCKTON and C. G. ELDREDGE.

THE fruit of the *Caulophyllum thalictroides*, blue cohosh, was gathered at Sylvan Beach, New York, August 21, 1907. It consists of drupes with a very thin pulpy layer. The drupes were green when first gathered, but on placing them in an air-bath at 105° they quickly turned blue, and became black as the drying slowly proceeded. They possess an odour something like that of bee-bread, were about the size of small marbles, and their average weight was about 0·2 grm. There were 296 grms. available for the analysis.

The Extraction of the Sugars.

One hundred grms. of the berries were placed in a 500 cc. flask, fitted with an inverted condenser. About 200 cc. of alcohol was added, and the flask was kept for ten hours on the hot-water bath. The alcoholic extract was poured into a second flask, and the alcohol distilled off. A gummy substance remained behind. The fruit was treated in this way for about seventy days, with as many different portions of alcohol, until the extract showed no further test for sugar with Fehling's solution. The alcohol which distilled over was colourless, but a sharp penetrating ethereal odour persisted. The odour of the syrupy residue was a mixture of caramel and liquorice, the latter especially noticeable when there was an inhalation far back in the nose and throat. The syrup had a bitter taste, and resembled liquorice when first taken into the mouth. The alcoholic extract and sugar solution both gave a decided acid reaction to litmus.

The effort was made to determine the amount of sugar by using Fehling's solution, the sugar equivalent of which was known. The result was somewhat unsatisfactory, but it was afterwards noticed that the fruit originally taken had

lost 40 per cent in weight. The kind of sugar was determined by the time of osazone formation. It was thus shown to be fructose. This was confirmed by crystallising from alcohol, when the melting-point of the purified crystals was found to correspond to that of fructose.

The Oils.

The nutlets from the original berries after the alcohol extraction, as described in the foregoing, were dried in the air-bath to remove all traces of alcohol. An attempt was made to crush the nutlets in a heavy agate mortar without success. They were next transferred to a large iron mortar. They proved to be very tough. Finally, by running them through a Taylor hand ore crusher ten or twelve times, they were reduced to a coarse powder. The particles of steel from the crusher were removed with a magnet.

The crushed nutlets were placed in a 250 cc. flask to which was attached an inverted condenser, and treated with fifteen successive portions of ether on the warm water-bath. The colouring matter had been mostly removed by the alcoholic treatment, and the oil from the ether was of a clear golden-brown colour. Two kinds of oil were obtained; one of a lighter hue than the other. The darker one was very volatile, and escaped before it could be tested. The odour of the golden-brown oil resembled that of olive oil.

One hundred grms. of the original fruit were crushed and treated with ether to extract the oils. This time the oils were dark green and light green in colour. When both were warmed on the water-bath the lighter coloured seemed to disappear, although the volume remained constant. A solid substance collected on the sides of the test-tube that contained the oils. Examined under the microscope, it was needle-shaped crystals, which were in too small quantity for identification. The green oils possessed an odour like the crushed fruit, but it is difficult to describe. The golden-brown oil and the green oil were both saponified, and the saponification equivalent agreed quite closely. The two are doubtless identical. In some respects the properties would place it in the laurin group, and in other respects it would seem to belong to the olein group. About 3 grms. of oil were obtained from 100 grms. of the fruit.

The Ash.

A portion of the crushed fruit was heated in a platinum dish. The odour resembled that of burning leaves. There resulted 0·0810 grm. of ash from 2·034 grms. of the fruit. This was separated in the usual way, and found to be:—

SiO_2	5·93	per cent of the ash
Fe_2O_3	1·97	,, ,,
CaO	10·74	,, ,,
MgO	2·35	,, ,,

Still another portion of ash by the J. Lawrence Smith method gave:—

K_2O	36·44	per cent of the ash
Na_2O	8·69	,, ,,

There was also found 30·61 per cent SO_3 and 3·67 per cent P_2O_5.

Other Substances.

The syrup which was extracted by the alcohol was found to contain small quantities of citric, tartaric, and tannic acids.

The Cornus Sericea.

The fruit of the *Cornus sericea* (*Kinnikinnik*) was gathered at Sylvan Beach, New York, September 6, 1906. It was found on shrubs about 10 feet in height. The fruit was dark blue in colour, and consists of a two-celled one-seeded drupe, each one twenty-third of a grm. in weight. There were 306 grms. of the air-dried fruit on hand for the investigation.

The Pulp.

Fifty grms. of the whole berries were placed in a 500 cc. flask, which was fitted with an inverted condenser, and treated with alcohol for three or four days on a warm water-bath until all colour was removed. Eight or ten portions of alcohol were required. The extract, which was amber to brownish in colour with a slight greenish cast, was transferred to a larger flask, and the alcohol removed by distillation. The distillate carried no odour of the fruit with it, and the remaining syrup had no distinctive odour.

A portion of the berries was also treated with water, yielding an extract of a darker colour than the alcohol. Some of this solution was treated with a relatively large amount of purified bone-black for fifteen to twenty hours on the water-bath, when it lost all of its colour. This solution yielded rather unsatisfactory results, and was finally discarded. A portion, however, was evaporated to dryness on the water-bath, when there was found a black residue on the sides of the dish and a number of small crystals in the centre. The crystals were shown to contain the bases potassium and calcium, and tartaric and oxalic acids, which seemed to be united with the bases to form acid potassium tartrate, acid potassium oxalate, with some calcium oxalate. The presence of potassium was apparent whenever any of the syrup, crystals, or fruit was held in the flame. The test was also confirmed with platinic chloride.

A portion of the water solution was cleared with basic lead acetate. In addition to the substances mentioned in the foregoing, there were found tannic, gallic, and malic acids.

The Sugars.

A portion of the filtrate from the basic lead acetate was evaporated to dryness on the water-bath with constant stirring. There were weighed out 0·2 grm. portions, which were treated according to the method of Sherman and Williams (*Journ. Am. Chem. Soc.*, May, 1906). The times of the trials pointed to fructose, with portions of 0·1, 0·05, 0·01, and 0·005 grm. The osazone was filtered off and purified by repeated crystallisations from alcohol. It was found to melt at 204—205°, which is the melting-point of both dextrose and lævulose. A microscopical examination of the crystals showed their identity with the osazone of the sugar found in the urine. The sugar is deliquescent, returning to a thick syrup on exposure to the air for a short time. The sugar is neither bitter nor astringent, but resembles molasses in taste.

The Nutlets.

The berries from which the sugar had been extracted were dried in the air-bath and ground in a coffee-mill. The moderately fine powder was treated with two solvents, alcohol and ether. The apparatus used was a 250 cc. flask, fitted with an inverted condenser; the treatment, first with alcohol, then ether, lasted several days. The ether was the better solvent, and extracted a light amber-coloured oil. This was treated with bone-black, which removed all colour. The pure oil on standing partially solidified, separating into two portions, one a solid at ordinary temperatures, the other a liquid. The solid part would again liquefy on a slight rise in temperature. On placing them in a freezing mixture no change was observed. We did not succeed in saponifying them. Judging from their physical characteristics the oils seemed to be palmitin and olein.

Substances Found.

Acid potassium tartrate, acid potassium oxalate, calcium oxalate, tannic, gallic, and malic acids, fructose, palmitin, and a small amount of gum.

We desire to thank Prof. Nicholas Knight for assistance in carrying on this work.

Cornell College, Mount Vernon, Iowa,
September 25, 1908.

FIFTEENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED DURING 1907.*

By F. W. CLARKE.

ALTHOUGH the number of new atomic weight determinations published during the year 1907 has not been large, the quality of the work done was remarkably high. Some of the determinations are of fundamental importance—as, for example, those of hydrogen, nitrogen, sulphur, potassium, and lead. Sulphur and lead are especially noteworthy, on account of their divergence from the older measurements. The data now available are as follows :—

Hydrogen.

Noyes has made complete syntheses of water in five series of determinations (*Journ. Am. Chem. Soc.*, xxix., 1718; CHEMICAL NEWS, xcvii., 56). The first series was defective, and is therefore not published by the author. For the other series very complete details are given, which would take too much space for repetition here. Noyes's corrected and final data are as follows :—

SECOND SERIES.—*Hydrogen from Sulphuric Acid, Weighed Twice.*

Weight H.	Weight O.	Weight H_2O.	At. wt. H.	
			H : O.	H : H_2O.
3·72565	29·57891	33·30408	1·00765	1·00767
3·80318	30·18400	33·98748	1·00800	1·00799
3·75873	29·83358	33·59127	1·00792	1·00795
2·96328	23·51987	26·48379	1·00792	1·00790
2·11395	—	18·89214	—	1·00795
3·53136	28·02910	31·56024	1·00791	1·00792
3·53959	28·09619	31·63554	1·00785	1·00786
		Mean	1·00787	1·00789

THIRD SERIES.—*Hydrogen from Sulphuric Acid, Oxidised by Copper Oxide.*

2·44279	19·39757	21·84042	1·00746	1·00746
2·18739	17·36305	19·55117	1·00784	1·00780
2·75129	21·84345	24·59389	1·00764	1·00768
4·00062	—	35·75073	—	1·00803
4·04057	32·07689	36·11762	1·00772	1·00772
		Mean	1·00767	1·00774

FOURTH SERIES.—*Hydrogen and Oxygen from Sulphuric Acid, combined by Palladium.*

2·27916	18·08455	20·36128	1·00823	1·00830
4·12734	32·76527	36·89043	1·00774	1·00780
4·17556	33·13449	37·30787	1·00818	1·00821
4·19346	33·27384	37·46453	1·00822	1·00831
2·30746	18·30863	20·61357	1·00825	1·00839
4·59692	36·48543	41·08162	1·00795	1·00797
4·63625	36·79354	41·42905	1·00806	1·00808
4·57274	36·28696	40·85834	1·00813	1·00817
		Mean	1·00809	1·00815

FIFTH SERIES.—*Hydrogen and Oxygen from Barium Hydroxide, combined by Palladium.*

4·61180	36·60909	41·22105	1·00779	1·00779
4·62358	36·69575	41·31647	1·00798	1·00806
4·59853	36·50484	41·10212	1·00776	1·00780
4·55832	36·17887	40·73904	1·00795	1·00790
4·20399	33·37000	37·57336	1·00782	1·00786
		Mean	1·00786	1·00788

The mean of all four series, assigned equal weight, is H = 1·00789.

The mean of the forty-eight determinations, as a single series, is H 1·00793.

The series, however, are not of equal weight, the second and fourth being better than the others. According to Noyes, the value H = 1·00787 is the most probable value to be derived from his determinations. Morley's classical syntheses of water, re-calculated, give H = 1·00762. Combining this with Noyes's results, the average is 1·00775, which is perhaps better than the determinations of either chemist taken alone.

Silver-Nitrogen.

Richards and Forbes (*Journ. Am. Chem. Soc.*, xxix., 808; CHEMICAL NEWS, xcvi., 180), in a most careful investigation, have effected the synthesis of silver nitrate from pure silver, and so measured the ratios between Ag and $AgNO_3$. The vacuum weights are given below, together with the ratio Ag : $AgNO_3$: : 100 : x.

Weight Ag.	Weight $AgNO_3$.	Ratio.
6·14837	9·68249	157·481
4·60825	7·25706	157·480
4·97925	7·84131	157·480
9·07101	14·28503	157·480
9·13702	14·38903	157·481
9·01782	14·20123	157·480
	Mean	157·480

A small correction for a trace of water retained by the nitrate reduces this figure to 157·479, which is identical with that obtained by combining all the older data. If now, Ag = 107·930, N = 14·037; but if the recent value for N, 14·008, is correct, then Ag becomes 107·880.

Potassium.

Richards and Mueller (*Journ. Am. Chem. Soc.*, xxix., 639; CHEMICAL NEWS, xcvi., 156) have re-determined the atomic weight of potassium by analyses of the bromide. (The paper is preceded by that of Richards and Staehler on potassium chloride, which was noticed in the report of this committee for 1206; it originally appeared in the *Berichte*). First, the ratio between silver bromide and the potassium salt was measured, with the subjoined results :—

Weight KBr.	Weight AgBr.	At. wt. K.
2·19027	3·45617	39·114
4·19705	6·62285	39·113
2·06723	3·26206	39·112
2·58494	4·07889	39·115
	Mean	39·1135

Second, the ratio between potassium bromide and metallic silver was determined by the usual titration method as follows :—

Weight KBr.	Weight AgCl.	At. wt. K.
4·33730	3·93164	39·113
4·18763	3·79587	39·115
4·15849	3·76943	39·116
3·67867	3·33450	39·116
3·60484	3·26776	39·110
4·78120	4·33387	39·118
5·67997	5·14860	39·116
6·41587	5·81571	39·115
2·88134	2·61184	39·113
3·64383	3·30309	39·111
3·12757	2·83504	39·113
	Mean	39·1143

The value for K was computed with Ag = 107·93 and Br = 79·953. All weights were reduced to a vacuum standard. The final value, obtained by combining these results with those of Richards and Stahler, is K = 39·1139. Clarke, in his "Re-calculation of the Atomic Weights,"

* From the *Journal of the American Chemical Society*, xxx., No. 3.

1897, from a combination of all the older data, found K = 39·112. The two values are nearly identical.

Sulphur.

The atomic weight of sulphur has been re-determined by Richards and Jones, who employed an entirely new method (*Journ. Am. Chem. Soc.*, xxix., 826; Chemical News, xcvi., 201). Silver sulphate was transformed into silver chloride by heating in gaseous hydrochloric acid. The weights, reduced to a vacuum, are subjoined. In the third column the chloride formed from 100 parts of sulphate is given :—

Weight Ag_2SO_4.	Weight AgCl.	Ratio.
5·21962	4·79859	91·934
5·27924	4·85330	91·932
5·08853	4·67810	91·934
5·36381	4·93118	91·934
5·16313	4·74668	91·934
5·08383	4·67374	91·933
5·13372	4·71946	91·931
5·16148	4·74490	91·929
5·19919	4·77992	91·936
5·37436	4·94088	91·934
	Mean	91·933

From this ratio, if Ag = 107·930 and Cl = 35·473, S = 32·113.

If Ag = 107·88 and Cl = 35·457, then S = 32·069.

Incidentally, the authors discuss the older values for sulphur, and especially those derived from gaseous densities. The latter they regard as subject to serious errors.

Lead.

In a preliminary paper, Baxter and Wilson give the results of their analyses of lead chloride (*Proc. Amer. Acad.*, xliii., 365). The data, with vacuum weights, are as follows :—

Weight $PbCl_2$.	Weight Ag.	Weight AgCl.	Atomic weight.	
			Ag ratio.	AgCl ratio.
4·67691	3·62987	4·82273	207·179	207·188
3·67705	2·85375	—	207·189	—
4·14110	3·21408	4·27016	207·173	207·192
4·56988	3·54672	—	207·185	—
5·12287	3·97568	5·28272	207·201	207·181
3·85844	2·99456	3·97949	207·186	207·136
4·67244	3·62628	—	207·189	—
3·10317	2·40837	3·19909	207·188	207·261
4·29613	3·33407	4·42982	207·202	207·204
		Mean	207·188	207·193

The mean of both series is Pb = 207·190 (see Note), when Ag = 107·93 and Cl = 35·473. This value is much higher than the usually accepted 206·9.

Note.—With Ag = 107·88, this becomes 207·090 (see *Journ. Am. Chem. Soc.*, xxx., 194).—Ed. *J. A. C. S.*

Palladium.

The determinations of Woernle (*Sitzungsb. Phys. Med. Soz. Erlangen*, xxxviii., 296) were based upon analyses of palladosamine chloride, $Pd(NH_3Cl)_2$. Two reductions in hydrogen gave the following results :—

Weight chloride.	Weight Pd.	Atomic weight Pd.
2·94682	1·48493	106·68
1·83140	0·92296	106·70

Five electrolytic determinations yielded the subjoined figures :—

Weight chloride.	Weight Pd.	Atomic weight Pd.
1·02683	0·51749	106·71
1·22435	0·61708	106·72
1·46735	0·73944	106·69
0·59796	0·30139	106·73
2·64584	1·33329	106·69
	Mean	106·708

All weights were reduced to vacuum. The antecedent values for H, N, and Cl are not stated.

Nickel and Cobalt.

Barkla and Sadler, studying the absorbability of secondary Röntgen radiations from various metals, which is an atomic function, find regularities to which nickel is an exception (*Phil. Mag.*, [6], xiv., 408; Preliminary Notice in *Nature*, Feb. 14, 1907; in *Nature* for April 4, Hackett questions the conclusions stated by Barkla). If, however, nickel be given a higher atomic weight than that now assigned to it, the anomalies disappear. Ten measurements of absorbability, compared with the absorbability of rays from other metals, gave, by interpolation, values for Ni between 61·15 and 61·6. These figures can hardly be assigned much weight in comparison with the excellent and more direct chemical determinations.

Parker and Sexton (*Nature*, August 1, 1907), in a brief note, announce that fifteen electrolytic comparisons of cobalt with silver give, in mean, Co = 57·7. The details of this investigation are yet to appear.

Indium.

Mathers (*Journ. Am. Chem. Soc.*, xxix., 485), in determining the atomic weight of indium, employed two methods. First, the ratio between $InCl_3$ and 3AgCl was measured gravimetrically, with the following results :—

Weight $InCl_3$.	Weight AgCl.	Atomic weight In.
2·11156	4·11421	114·80
4·95920	9·64176	114·85
1·98175	3·85125	114·95
5·54540	10·77904	114·90
1·46361	2·84557	114·86
4·08602	7·94054	114·96
	Mean	114·88

Secondly, similar analyses were made of indium tribromide, as follows :—

Weight $InBr_3$.	Weight AgBr.	Atomic weight In.
2·73494	4·34550	114·89
7·69880	12·23341	114·86
6·27450	9·96917	114·89
5·36642	8·52741	114·85
5·16112	8·20128	114·85
4·98336	7·92009	114·81
	Mean	114·86

The calculations were made with Ag = 107·93, Cl = 35·473, and Br = 79·953. The author favours In = 114·9 as the value to be accepted.

(To be continued).

Physical Society.—A Meeting of the Society will be held on Friday, Oct. 23rd, at the National Physical Laboratory, Bushy House, Teddington, by kind invitation of Dr. R. T. Glazebrook, F.R.S., Director of the Laboratory. It is proposed to show a series of demonstrations of work in progress in the Laboratory, which will be on view from 3.30 p.m. onwards. To give some idea of the probable number of visitors, the Director would be glad if Fellows proposing to attend or to bring visitors would intimate their intention to him by post-card, as far as they conveniently can, by Monday, Oct. 19th. He hopes, however, that no one will be deterred from coming through his having been unable to comply with this request.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

PART III.—ANALYSIS OF THE ALUMINIUM AND IRON GROUPS, INCLUDING BERYLLIUM, URANIUM, VANADIUM, TITANIUM, ZIRCONIUM, AND THALLIUM.

By ARTHUR A. NOYES, WILLIAM C. BRAY, and ELLWOOD B. SPEAR.

(Continued from p. 184).

Confirmatory Experiments and References.

G. D., Section 1: Precipitation of Zinc with Chromium on adding NH_4OH.—Ten mgrms. Zn as $ZnCl_2$ and 100 mgrms. Cr as $KCr(SO_4)_2$ were dissolved in 4 cc. HCl (1·12) and 96 cc. water; 10 cc. NH_4OH (0·96) were added a little at a time to the cold mixture (giving an excess of about 3 cc. NH_4OH); after three or four minutes the precipitate was filtered off, the filtrate, which had a very faint pink colour, was heated to boiling, and the precipitate that separated (estimated to contain 2 or 3 mgrms. Cr) was filtered off. H_2S was finally passed into the alkaline filtrate; no precipitate separated, thus showing that the zinc had been completely carried down with the $Cr(OH)_3$. The precipitates were united and dissolved in HCl, and the solution treated by P. 52 to 57; the zinc was precipitated as ZnS in P. 57.

For the preparation and properties of $ZnCr_2O_4$, see Chancel (*Comptes Rendus*, 1856, xliii., 927), Viard (*Bull. Soc. Chim.*, 1889, [3], ii., 331).

Action of NH_4OH *and* $(NH_4)_2S$ *on Nickel Solutions, and Precipitation of* NiS *on boiling the Brown Solution.*—See C. E., P. 51, N. 12.

The Test for Vanadium with H_2S.—See C. E., P. 51*a*, N. 1.

The Slow Reduction of Vanadic Acid to Hypovanadic Acid by H_2S.—Fifty mgrms. V as H_3VO_4 were dissolved in 4 cc. HCl and 100 cc. water; the mixture was saturated with H_2S in the cold. After about ten minutes the mixture was filtered several times to remove the sulphur that had separated, and the blue filtrate was heated to boiling; a large precipitate of sulphur separated, showing that reduction was more rapid at higher temperatures. The mixture was filtered, and the hot filtrate again saturated with H_2S; a large precipitate of sulphur separated. After ten minutes the mixture was boiled, filtered, and again saturated with H_2S; sulphur separated, showing that the reduction was still incomplete. The treatment of the hot solution with H_2S was repeated, the sulphur filtered off, the mixture was boiled in a casserole to expel H_2S, and 1 grm. KI was added; no iodine was liberated, showing that the reduction to hypovanadic acid was complete. The first experiments were repeated with 3 cc. HNO_3 (1·20) in 100 cc.: the results were the same.

Reduction of Vanadic Acid to Hypovanadic Acid by HCl (1·20).—See Gooch and Curtis (*Am. Journ. Sci.*, 1904, [4], xvii., 41). The reaction is slow in the cold but rapid on heating. When a moderate amount of vanadium is present, the reduction is not absolutely complete unless a more concentrated HCl solution is used than that obtained on evaporating. Compare C. E., *P. 58*d*, N. 1.

Action of NH_4OH *on a Hypovanadate.*—100 mgrms. V as Na_3VO_4 were treated with H_2S by P. 21 to reduce it to the hypovanadic state; the solution was evaporated to about 40 cc., and made alkaline with NH_4OH; a dirty grey precipitate separated. Fifty mgrms. V as Na_3VO_4 were boiled with concentrated HCl (1·20) to reduce the vanadium; the mixture was diluted to 100 cc., and made alkaline with NH_4OH; a small grey precipitate, with a greenish shade, separated. Several cc. NH_4OH were added; the precipitate dissolved.

Precipitation of Vanadium in P. 51 or by NH_4OH *alone when Iron or Zinc is present.*—500 mgrms. Fe as $FeSO_4$ and 100 mgrms. V as Na_3VO_4 were treated with H_2S by P. 21, evaporated to 40 cc., and treated by P. 51; the filtrate was tested for vanadium by *P. 51*a*; less than 1 mgrm. V was found. The experiment was repeated with 500 mgrms. Fe and 10 mgrms. V; no vanadium was found in the filtrate.

500 mgrms. Fe as $FeCl_3$ and 100 mgrms. V as Na_3VO_4 were dissolved in 40 cc. containing 4 cc. HCl (1·12), the solution was made alkaline with NH_4OH, and, without adding $(NH_4)_2S$, the mixture was filtered, and the filtrate was tested for vanadium by *P. 51*a*; only a trace of vanadium was found. The experiment was repeated with 500 mgrms. Fe as $FeSO_4$ and 100 mgrms. V as Na_3VO_4; the mixture was allowed to stand, and shaken frequently in order that the iron might be completely precipitated; no vanadium was found in the filtrate. Fifty mgrms. Fe as $FeCl_3$, 15 mgrms. V as hypovanadic acid, and several grms. NH_4Cl were dissolved in a little HCl and 100 cc. water; the solution was made alkaline with NH_4OH, and the filtrate was evaporated to dryness, ignited, dissolved in a little NCl, and tested for vanadium by P. 51*a*; only a trace of vanadium was found. Therefore vanadium is almost completely carried down when a three- to fivefold excess of iron is present.

300 mgrms. Zn as $ZnCl_2$ and 10 mgrms. V as H_3VO_4 were treated with H_2S by P. 21, evaporated to 30 cc., and treated by P. 51; the filtrate was tested for vanadium by *P. 51*a*; 3 or 4 mgrms. V were found. The ZnS precipitate was analysed by the regular procedure; the remainder of the vanadium was found.

Reduction of Vanadic Acid by HI *and its subsequent behaviour with the Group Reagents.*—According to Gooch and Curtis (*Am. Journ. Sci.*, 1904, [4], xvii., 45), the first stage of the reduction, that to V_2O_4, took place rapidly in a dilute HI solution, but the second stage, that to V_2O_3, takes place slowly, and only in hot concentrated solutions. When a mixture containing 60 mgrms. V_2O_3, 1 grm. KI, and an excess of HCl was evaporated to 2 cc., about 97 per cent of the vanadium was reduced to a salt corresponding to V_2O_3.

In our experiments 1 mgrm. V as Na_3VO_4 was dissolved in 15 cc. HCl (1·20) in a 50 cc. round bottom flask; 1 grm. NH_4I was added, and the mixture was evaporated carefully to 2 or 3 cc., a capillary ebullator tube being used to prevent bumping. The mixture was diluted with 10 cc. water, and NH_4OH (0·96) was added until the solution after shaking smelled distinctly of it; a dark green precipitate formed. A few drops colourless ammonium sulphide were added; the precipitate did not dissolve. It was filtered off, and dissolved in a little HNO_3; a large excess (5 to 10 cc.) of NH_4OH (0·90) was added, and the mixture saturated with H_2S; the solution became red, showing the presence of vanadium. The filtrate from the NH_4OH precipitate was tested for vanadium in the same way; only a very small amount was found. The experiment was repeated, except that the evaporated mixture was diluted to 20 cc.; more vanadium was found in the filtrate than in the precipitate. The experiment was repeated, the mixture being diluted to 40 cc.; all the vanadium was found in the filtrate.

The experiment was repeated several times with 100 mgrms. V, the mixture being diluted to 20 cc. after the evaporation; on adding NH_4OH a dark coloured (brown) precipitate separated, but it dissolved completely or in large part on adding a few drops of colourless $(NH_4)_2S$.

The experiment was repeated with 50 mgrms. V; after the first evaporation 15 cc. HCl (1·20) and 1 grm. NH_4I were added, and the evaporation repeated; the mixture was diluted to 50 cc.; a large dark greenish coloured precipitate separated on the addition of NH_4OH, and it did not dissolve on adding several drops $(NH_4)_2S$. The filtrate was evaporated nearly to dryness; an excess of 5 cc NH_4OH (0·90) was added, and the mixture saturated with H_2S; not more than 0·5 mgrm. V was found in the filtrate. The last experiment was repeated with 5 and with 10 mgrms. V; in the experiment with 5 mgrms. only a very slight precipitate was obtained on adding NH_4OH, and it quickly re-dissolved; with 10 mgrms. a precipitate

* From the *Journal of the American Chemical Society*, xxx., No. 4.

was obtained, but about half the vanadium was found in the filtrate. Therefore in a volume of 50 cc. the precipitation is fairly satisfactory for large amounts of vanadium, but not for small amounts. The above results were not perfectly reproducible, but each of them was obtained several times.

A number of attempts were made to reduce 50 to 100 mgrms. V as Na_3VO_4 by evaporating as described above with 10 to 15 cc. pure concentrated HI, and to precipitate the vanadium with NH_4OH after diluting to 40 or 50 cc.; but the precipitation was much less complete than after the reduction with NH_4I and HCl, probably owing to the larger proportion of iodine found to be retained in the solution in the former case. The experiments were repeated with HI that had been exposed to the air, and contained much iodine; the precipitation was still less complete.

Rate of Oxidation of Trivalent Vanadium in the presence of NH_4OH *and of* $(NH_4)_2S$.—Fifty mgrms. V was reduced twice by evaporation with 15 cc. HCl (1·20), and 1 grm. NH_4I to 2 or 3 cc.; the residue was diluted to 50 cc., and made alkaline with NH_4OH. The mixture was divided into two parts; one was filtered at once, and the second after half-an-hour; both filtrates were tested for vanadium by *P 51*a*; a very poor test was obtained in the first filtrate, and a good one in the second. The experiment was repeated, except that the second portion was filtered after two hours; the first filtrate gave a slight test for vanadium; the second contained 2 to 4 mgrms. V. Therefore the oxidation takes place slowly in the presence of NH_4OH.

The experiments were repeated, except that several drops colourless $(NH_4)_2S$ were also added; the filtrates obtained at once, after half-an-hour, and after two hours gave only slight tests for vanadium. Therefore the addition of a little $(NH_4)_2S$ does not cause the vanadium hydroxide to dissolve, and the rate of oxidation is slower in the presence of $(NH_4)_2S$ than in that of NH_4OH alone.

The oxidation, by the oxygen of the air of the trivalent vanadium after dilution, is therefore much too slow to account for the abnormal results, such as the nearly complete precipitation of 50 to 100 mgrms. V in one experiment, and the non-precipitation in another performed under apparently the same condition.

G. D., Section 2: Action of HCl *on* NiS *or* CoS.—Herz (*Zeit. Anorg. Chem.*, 1901, xxvii., 390, and xxviii., 343) treated sulphides which had been kept on filters for several days after precipitation with 0·5 normal HCl (1 vol. HCl, 1·12, and 12 vols. water), and found that the evolution of H_2S could not be detected by odour, or by action on paper moistened with a lead salt. On the other hand, he found H_2S to be evolved fairly rapidly by the action of 0·5 normal HCl on freshly precipitated sulphides. He concludes that there are two alloptropic forms of the sulphides, one that is soluble in 0·5 normal HCl, and one that is not. As Glixelli (*Zeit. Anorg. Chem.*, 1907, lv,, 297) has pointed out, this evidence of decreased solubility is not very conclusive, for the reaction with the old sulphides may simply be much slower. The following experiments show that NiS, at any rate while freshly precipitated, is not a mixture of two sulphides differing markedly in solubility.

200 mgrms. Ni as NiS, precipitated in the cold by passing H_2S into NH_4OH solution, was digested in the cold for a known time with about 30 cc. dilute HCl (1 vol. HCl, 1·12, and 5 vols. water). The HCl was first saturated with H_2S, and H_2S was passed through the mixture in a small flask during the treatment. The mixture was filtered, and the experiment repeated several times with the NiS residue. The amount of nickel dissolved in each treatment was estimated by adding NH_4OH, and precipitating the nickel as NiS by passing in H_2S. In the first treatment of fifteen minutes about 20 mgrms. Ni dissolved; in each of the next four treatments of fifteen minutes each, steadily decreasing amounts of Ni dissolved, and in the fifth treatment the amount was estimated to be 10 mgrms. Ni. The sixth and seventh treatments were each for half-an hour; somewhat more nickel dissolved than in the fifth treatment of fifteen minutes. The eighth treatment was for four hours, nearly as much dissolved as in the first treatment (say, 18 mgrms.). Over-night, without passing the current of H_2S, about 20 mgrms. Ni dissolved. In a last treatment for six hours, 25 or 30 mgrms. dissolved. The final residue contained only about 30 mgrms. Ni. A similar series of experiments was performed, except that the HCl was not saturated with H_2S, and no H_2S was passed through the mixture; the results were similar except that the NiS dissolved more slowly owing to the fact that the mixture was very little stirred.

100 mgrms. Ni as NiS (precipitated by H_2S in NH_4OH solution) were digested with 30 cc. dilute HCl (1 vol. HCl, 1·12; and 3 vols. of water), for five minutes; about 5 mgrms. Ni dissolved. The experiment was repeated with HCl (1·12); the amount of Ni that dissolved was not much greater than in the preceding experiment. The last experiment was repeated with 1 mgrm. Ni; only a small proportion of the nickel dissolved.

Action of HCl *on* NiS *when other Sulphides are also present.*—500 mgrms. Fe as $FeSO_4$ and 5 mgrms. Ni as $NiSO_4$ were dissolved in 50 cc. water containing 2 cc. H_2SO_4 (1·84), and the solution treated at about 40° with NH_4OH and $(NH_4)_2S$ as described in P. 51; the filtrate was clear and light coloured, showing that it contained no nickel. The precipitate was dried by suction, and treated in a casserole with 30 cc. cold dilute HCl (1 vol. HCl, 1·12; and 5 vols. water), with frequent stirring, for five minutes; only a very small black residue remained, which was found to contain about 0·5 mgrm. Fe but no nickel. The experiment was repeated, except that ferric chloride was used instead of ferrous sulphate; the residue contained 1 or 2 mgrms. Fe and a mere trace of nickel. Both experiments were repeated, except that the sulphides were precipitated at about 90° by passing H_2S into NH_4OH solutions. In the experiment with ferrous iron the residue insoluble in dilute HCl contained nearly 1 mgrm. Fe and less than 1 mgrm. Ni; in the experiment with ferric iron the residue contained about 1 mgrm. Fe and nearly all the nickel. The last experiment was repeated with 500 mgrms. Fe as $FeCl_3$ and 2 mgrms. Ni as $NiSO_4$; the residue insoluble in cold dilute HCl contained a little iron and nearly all the nickel. The first of the above experiments was repeated with 500 mgrms. Fe as $FeSO_4$ and 10 mgrms. Ni as $NiSO_4$; the residue insoluble in dilute HCl, and also the filtrate were tested for iron and nickel; the residue contained about 1 mgrm. Fe and 5 mgrms. Ni; the HCl solution contained also about 5 mgrms. Ni. The experiment was repeated, except that the sulphides were precipitated at about 90° by passing H_2S into an NH_4OH solution; the residue insoluble in dilute HCl contained about 0·5 mgrm. Fe and 3 or 4 mgrms. Ni.

500 mgrms. Mn as $MnSO_4$ and 5 mgrms. Ni as $NiSO_4$ were dissolved in 2 cc. H_2SO_4 (1·84) and 50 cc. water, and the solution was treated with NH_4OH and $(NH_4)_2S$ as described in P. 51; the filtrate was clear, showing the absence of nickel. The precipitate was digested with 30 cc. cold dilute HCl (1 vol. HCl, 1·12; and 5 vols. water), with frequent stirring, for five minutes; the small dark coloured residue on analysis was estimated to contain 3 or 4 mgrms. Ni; the HCl solution contained only about 0·5 mgrm. Ni.

The experiment was repeated with 500 mgrms. Zn as $ZnSO_4$ and 2 mgrms. Ni as $NiSO_4$; after ten minutes' treatment with the dilute HCl a very large residue remained; the HCl solution contained only about 100 mgrms. Zn, and no Ni. The second treatment with HCl lasted over-night: about 300 mgrms. Zn and no Ni dissolved. The third treatment lasted two days; the residue was small and dark coloured, and contained over 1 mgrm. Ni and little or no Zn; the HCl solution contained about 100 mgrms. Zn and a little Ni. The experiment was repeated with HCl (1·12); a black residue remained.

These experiments show that small amounts of NiS may be dissolved completely when distributed throughout a

large precipitate of iron sulphide, but that they are not readily dissolved in the presence of ZnS or MnS. They also show that ZnS dissolves slowly in dilute HCl just as NiS does.

(To be continued).

OBITUARY.

MR. JOHN TREVOR CART.

WE regret to have to record the death of Mr. John Trevor Cart. Mr. Cart entered the School of the Pharmaceutical Society in October, 1902, as Bell Scholar—the chief distinction open to pharmaceutical students after the completion of their apprenticeship. He had served for three years in a pharmacy at Shrewsbury, and, as he had passed the "Minor" or qualifying examination of the Society before entering the School, he was granted special permission to pursue advanced studies, which led successively to his passing the "Major" examination of the Society in April, 1903; to his appointment as Demonstrator in Chemistry in October, 1903, and to his selection as Demonstrator in Pharmaceutics in April, 1904—a post which he held until he took up an appointment with the firm of Hopkin and Williams in July, 1905. There he gained additional experience in analytical and manufacturing chemistry under the supervision of Mr. Edmund White, leaving in 1906 for Newcastle-on-Tyne, where he was appointed chemist to Messrs. C. A. Parsons and Co., to carry on chemical engineering research work, and to deal with such chemical questions as arise in the carrying on of engineering and electrical business generally. He soon formed close friends with his colleagues and managers, who were attracted by his unselfish and enthusiastic nature, and his knowledge in the domain of chemistry. His work while at Newcastle threw him much into contact with Mr. Charles A. Parsons and others, who held him in their highest regard. To all who had the privilege of his acquaintance and friendship, his sudden and untimely death has come as a great shock and sorrow.

Mr. Cart was a B.Sc. of London University, an Associate of the Institute of Chemistry, and a member of the Northern Scientific Club.

Prof. W. Palmer Wynne, F.R.S., of Sheffield, says:—"During my career as a teacher I have known few more brilliant workers among my students, and none of a more amiable and unselfish disposition."

NOTICES OF BOOKS.

The Analysis of Ashes and Alloys. By L. PARRY, A.R.S.M. London: *The Mining Journal.* 1908.

THE notes on various analyses in this book will serve to recall to the chemist who is thoroughly conversant with the theory and practice of assaying details with which he cannot burden his memory, and will also give him some suggestions which he may find of value as to the relative accuracy or rapidity of different methods. At the same time the student who attempts to use it as a laboratory guide during his course of analysis will find it maddening. Details are often slurred over or even altogether omitted; many important points are left to the judgment or intelligence of the worker when he most needs some guide, and even methods of great value are left out or references to other works are given for them. However, regarded as merely outlined notes the book has good points. The directions are exceedingly concise, and the substances treated are numerous. Section I. describes the assay of the commonest metals in alloys, &c., care being taken to weigh thoroughly the merits of as many different methods as is practicable. In Section II. the analyses of ashes and slags is treated, and general methods of sampling and testing alloys are described. Section III. gives a summary of miscellaneous analyses, and in addition contains some notes on standard solutions, as well as tables of useful numerical and other data.

Der Betriebs-Chemiker. ("The Works' Chemist"). By Dr. RICHARD DIERBACH. Second Edition. Berlin: Julius Springer. 1908.

THIS book comprises a collection of notes, somewhat amplified, made by the author during his experience as a works' chemist. Thus it is essentially a practical work, and meant not for the use of students but of practical men. Moreover, it does not treat more particularly of any special branch of chemical technology, but is of a general nature, discussing problems which occur in different aspects in all industries. The cost of apparatus and materials is continually referred to, and every effort has been made to make the book of real value to the chemist. This aim is on the whole well fulfilled, and the fact that the book has found some measure of general acceptance is testified by the appearance of a second edition comparatively soon after the first.

Der Dampf in der Chemischen Technik. ("Steam in Technical Chemistry"). By W. MOMBER. Halle-a-S.: Wilhelm Knapp. 1908.

WHEN the student of chemistry has just finished his technical course and is taking a post in works or factory he frequently finds that he is required to solve problems of a very different nature from those he has investigated in the laboratory, and that his practical work does not seem to have been altogether suitable training for him. The object of this and other monographs of the same series is to bridge over this gap between works and laboratory as far as possible, and give the student a firm footing with regard to the applications on a large scale of operations and methods with which he is perfectly familiar in the laboratory. The subject treated of in this volume is of great importance, for steam is widely used in industrial chemistry for drying and heating purposes, and it is a matter of difficulty to decide what to omit, what to discuss in outline, and what to treat fully. This difficulty the author has met successfully, and the book should give the chemist very material assistance in understanding the uses of steam in the works. Different methods of producing and utilising it are described in outline, and the processes of distillation, rectification, &c., are discussed with illustrations of typical apparatus.

Die Chemische Analyse. ("Chemical Analysis"). Edited by Dr. B. M. MARGOSCHES. Vols. IV., V. By Dr. Ing. A. FISCHER. Stuttgart: Ferdinand Enke. 1908.

THE rapid methods of analysis by electrolysis which have been perfected in recent years are excellently described in his book. The general theory of electrolytic analysis as applied to the estimation and separation of various substances is first treated, and a short account is given of the apparatus used and its manipulation, although for fuller details the student is advised to refer to text-books of electro-chemistry. Some points which are of particular importance in this branch of electro-chemistry (for example, the different shapes which the electrodes may be made to assume) are considered in detail in fully illustrated discussions. In the practical part, tabulated schemes show the experimental conditions under which the electrolyses are performed, full information being given as to current, voltage, temperature, duration of experiment, &c., and the results of typical analyses are also tabulated. The author's extensive experience in practical electro-chemistry enables him to give valuable advice as to choice of methods, and some hitherto unpublished experiments performed by him are described.

Quantitative Analyse durch Elektrolyse. ("Quantitative Analysis by Electrolysis"). By ALEXANDER CLASSEN. Fifth Edition. Berlin: Julius Springer. 1908.

THE prominent part taken by the author of this treatise in the working out of methods of analysis by electrolysis fully warrants the recognition of his work as a classic upon the subject, and since its first appearance twenty-six years ago it has maintained its place as the authoritative standard work of reference. Each fresh edition has included a considerable amount of new matter, but perhaps none of them has been so much extended as the fifth, which may almost be regarded as a completely new work. The more important parts, in which great alterations have been made, include the descriptions of rapid methods of estimation, the arrangements in use at the Technical High School at Aachen being fully described. Moreover, improved methods of separating and determining the halogens, the alkaline metals, and the metals of the alkaline earths are discussed, while a new section has been added on practical applications of electro-analysis in the treatment of alloys and ores.

Jahresbericht Uber die Fortschritte des Zeugdrucks und Verwandter Industrien. ("Annual Report on the Progress of Fabric Printing and Allied Industries"). Vol. I. Edited by Prof. ANTONIO SANSONE. Leipzig: Gustav Fock. 1908.

DESCRIPTIONS of improved processes and apparatus in calico printing are published in such great numbers, and are so widely scattered in different periodicals in all languages, that the chemist finds it exceedingly difficult to keep pace with the most modern developments. Hence the value of this publication will be at once recognised, and provided that it performs its work of selection judiciously it should find a ready welcome among the readers to whom it specially appeals. The reports will be published annually, and will give a review of all matters of interest relating to cotton-printing, bleaching, and dyeing. The first number contains introductory articles, and also short chapters on the manufacture of artificial colouring matters, and on the use of the indigo-red B and thioindigo-scarlet R, the last paper being illustrated by sample patterns which have been dyed according to special formulæ given in the text.

CORRESPONDENCE.

THE THERMO-CHEMISTRY OF ALUMINIUM.

To the Editor of the Chemical News.

SIR,—Some time ago I was led to surmise that in combustion the greater portion of the heat might be given out by oxygen.

I communicated to the CHEMICAL NEWS several papers containing the theoretical reasoning leading to this, and again approach the subject of thermo-chemistry with a view to its technical application.

Aluminium when used in metallurgical processes gives out great heat.

The reaction taking place is represented by Equation I.

I. $Fe_2O_3 + Al_2 = Fe_2 + Al_2O_3 +$ . . . .
II. $Al_2O_3, yH_2O + 388{\cdot}920$
III. $Fe_2O_3, yH_2O = 191{\cdot}150$

I should surmise that the data given in Equation II. and III. represent the heat given out in Equation I., the difference being 197·770 cals.

This, though merely suggested, may be of use to such metallurgical chemists as use thermite or similar preparations.—I am, &c.,

J. C. THOMLINSON.

6, Villa View, Low Fell, Gateshead.

TENDERING FOR PUBLIC APPOINTMENTS.

To the Editor of the Chemical News.

SIR,—May we ask you to be good enough to insert in the forthcoming issue of your journal the following resolution, which was unanimously passed at a special Council Meeting of the Society of Public Analysts and other Analytical Chemists, held on the 1st inst.—We are, &c.,

ALFRED CHASTON CHAPMAN,
P. A. ELLIS RICHARDS, } Hon. Secretaries.

Resolution.

The Council of the Society of Public Analysts and other Analytical Chemists has had under consideration the practice, which has been adopted recently by certain Public Bodies, of inviting applicants for the Office of Public Analysts to state the terms upon which they are prepared to accept such appointments.

The Council is of opinion that it is against the interests of the public, and degrading to the profession of Analytical Chemistry for appointments to be offered "on tender," and calls upon the Members of the Society to resist the practice.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvii., No. 9, August 31, 1908.

Dissociation Temperature of Ammonia and Carbon Monoxide.—Hermann C. Woltereck.—When pure ammonia gas is passed through a glass tube which is raised to a high temperature, the first traces of dissociation are observed at 620°, and the mixture of gases issuing from the tube becomes explosive below 630°. The decomposition of ammonia by metallic iron begins at 320°, and by iron oxide at 420°. The dissociation of carbon monoxide begins between 570° and 580°; it does not occur in presence of a trace of water-vapour even at very high temperatures.

Berichte der Deutschen Chemischen Gesellschaft, Vol. xli., No. 12, 1908.

Reaction between Ammonium Persulphate and Sodium Peroxide.—R. Kempf and Ed. Oehler.—When an alkaline aqueous solution of ammonium persulphate is allowed to stand, large quantities of nitric acid are formed, the ammonia set free by the alkali being oxidised almost quantitatively at the ordinary temperature to nitric acid. But if silver peroxide is allowed to act on alkali persulphate the free ammonia is oxidised to nitrogen. Thus the stronger oxidising agent oxidises the ammonia to the lower stage of oxidation. This phenomenon can be explained by the law of successive reactions, according to which in a slow reaction the final stable reaction products are obtained, while a rapid reaction yields less stable provisional products. Thus, nitrogen is the unstable intermediate product, and nitric acid is the stable final product. Silver peroxide oxidises large quantities of ammonia in a few seconds, while sodium persulphate takes four days to produce 0·6 grm. of nitric acid. Sodium peroxide, even in the solid dry state, reacts energetically with ammonium persulphate, the reaction being accompanied by the development of much heat and light, and sometimes by an explosion. The analytical study of the reaction shows that several chemical reactions proceed simultaneously. Thus ammonia is set free, and this is oxidised to nitrogen, as shown by the equation $(NH_4)_2S_2O_8 + 2Na_2O_2 = 2Na_2SO_4 + 4H_2O + N_2$. The heat

evolved by this reaction decomposes the oxidising agent, especially the sodium peroxide, and oxygen is evolved. No explosive mixture is obtained if the sodium peroxide is replaced by caustic soda, or if instead of ammonium persulphate, ammonium sulphate or sodium persulphate is used.

Hydrogen Persulphide.—Rudolf Schenck and V. Falcke.—To prepare hydrogen persulphide potassium polysulphide solution is poured into concentrated hydrochloric acid, and the clear light yellow oil thus formed is separated from the aqueous liquid, and washed with dilute hydrochloric acid. The oil can be dried with calcium chloride, and distilled off from the drying agent in a vacuum, the vessels in which the raw sulphide is distilled having previously been carefully freed from traces of alkali. Thus a strongly refracting oil is obtained with a characteristic odour, recalling that of camphor. The substance is very volatile and also very labile, readily splitting up in presence of small quantities of alkali into sulphur and sulphuretted hydrogen. Hydrogen persulphide is dissolved by carbon disulphide, benzene, alcohol, and ether, but is readily decomposed by solvents into sulphur and sulphuretted hydrogen. The composition of the persulphide may be determined by decomposing it completely into sulphur and sulphuretted hydrogen by means of ether, and estimating the amount of each constituent. The results obtained agree very well with the formula H_2S_3, and this formula is confirmed by molecular weight determinations in which the depression of the freezing-point is measured, bromoform being used as solvent.

Bromination Experiments with Diazobenzene Perbromides.—Carl Bülow and Herm Schmachtenberg.—At a low temperature diazobenzene perbromide is readily dissolved by acetone and acetophenone. From the solution hydrobromic acid is evolved, and a crystalline mass of pure benzenediazonium bromide is formed, while at the same time the unmistakable odour of monobromacetone or acetophenone may be recognised. The yield is quantitative as expressed by the equations:—

$$C_6H_5.N_2.Br.Br_2 + CH_3.CO.CH_3 = C_6H_5.N_2.Br + CH_3.CO.CH_2Br + HBr,$$

$$C_6H_5.N_2Br.Br_2 + CH_3.CO.C_6H_5 = C_6H_5.N_2.Br + CH_2Br.CO.C_6H_5 + HBr.$$

The perbromide acts upon acetic acid solutions of unsaturated compounds, such as cinnamic or phenylpropiolic acids, giving the dibrom addition products:—

$$C_6H_5.N_2.Br.Br_2 + C_6H_5.CH{:}CH.COOH = C_6H_5.N_2.Br + C_6H_5.CHBr.CHBr.COOH,$$

$$C_6H_5.N_2.Br.Br_2 + C_6H_5.C{:}C.COOH = C_6H_5.N_2Br + C_6H_5.CBr{:}CBr.COOH.$$

With an alcoholic solution of aniline the perbromide gives chiefly the hydrobromide salt of the base, diazoamidobenzene and small quantities of amidoazobenzene and tribromphenol. Similar results are obtained with acetyl-*p*-amidobenzenediazonium bromide.

Crystallised Boron.—Heinrich Biltz.—Kühne stated that silicon and boron are obtained in the crystailine form if their oxides are burnt with aluminium and sulphur; part of the aluminium forms sulphide, and thus sufficient heat is generated to decompose the oxide with the rest of the aluminium. The boron crystals are then said to be easily isolated from the aluminium sulphide. The author has repeated Kuhne's experiments, and by an improvement of the method has obtained black crystals resembling those described by Wöhler and Deville in 1857. These authors obtained, besides the black crystals, clear yellow or brown crystals containing boron, aluminium, and carbon. They regarded the two crystalline forms as essentially identical, and thought they were elementary boron, containing carbon and aluminium as impurities. The author's experiments have shown that in the black crystals a chemical compound, an aluminium boride of formula AlB_{12}, is present.

Velocity of Reaction of Bromine on Benzaldehyde.—W. Herz and Hermann Dick.—Bromine and benzaldehyde yield brombenzylbenzoate,—

$$2C_6H_5.COH + Br_2 \quad C_6H_5.CO.O.CHBr.C_6H_5 + HBr.$$

It is *à priori* probable that the transposition is a bimolecular reaction, according to the equations:—

$$C_6H_5.COH + Br_2 = C_6H_5.COBr + HBr,$$
$$C_6H_5COBr + C_6H_5.COH \quad C_6H_5.CO.O.CHBr.C_6H_5.$$

To test this hypothesis the authors have determined the constant K from the bimolecular reaction formula $\frac{1}{t(A-B)} \log \frac{B(A-x)}{A(B-x)} = K$, and have obtained results which agree very well with the theoretical value. The values of K are independent of the concentrations within certain definite limits.

MEETINGS FOR THE WEEK.

WEDNESDAY, 21st.—Microscopical, 8. "The Mouth-parts of the Nemocera and their relation to the other Families in Diptera—Corrections and Additions to the Paper published in 1904," by W. Wesché. "Resolution of Periodic Structures" and "An Auxiliary Illuminating Lens," by E. M. Nelson.

FRIDAY, 23rd.—Physical, 3.30 (at the National Physical Laboratory, Bushy House, Teddington).

THURSDAY, 22nd.—Chemical, 8.30. "Passage of Hydrogen through a Palladium Septum, and the Pressure which it Produces," by T. Tsakalotos. "Relationship of Colour and Fluorescence to Constitution—Part II., Rhodamines of Mellitic Acid," by O. Silberrad and C. S. Roy. "Constitution of the Fluorescences of Mellitic and Pyromellitic Acid," by O. Silberrad. "A New Form of Gas Burette," by A. E. Hill. "Molecular Compound of Trinitroacetaminophenol and β-Naphthol," by R. Meldola and J. G. Hay. "Reduction Products of Azoxybenzene," by L. H. Berry. "Constitution of the Salts of Phthaleins, and the Cause of Colour in the Triphenylmethane Series," by A. G. Green. "Chlorination of *p*-Nitraniline," by B. Flürscheim. "Relation between Absorption Spectra and Chemical Constitution—Part X., Unsaturated Acids of the Benzene Series," by E. C. C. Baly and K. Schaefer. "Condensations with Monochloromethyl Ether—Part I., Condensation of Monochloromethyl Ether with Ethyl Malonate and Ethyl Isopropyl Malonate," by J. L. Simonsen. "Relation between Chemical Constitution and Physiological Action in Certain Substituted Aminoalkylesters," by F. L. Pyman. "Effect of Constitution on the Optical Rotatory Power of Optically Active Nitrogen Compounds," by R. W. Everatt and H. O. Jones.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

"Official Methods of American Agricultural Chemists."—(Reply to "X.").—This can be obtained by writing to the Director, U.S. Department of Agriculture, Washington, D.C. All such publications are on sale (at prices varying from 5 to 15 cents), obtainable from the superintendent of Documents, Government Printing Office, Washington, D.C.—KATHARINE A. WILLIAMS.

ENGINEERING CHEMIST,

SWiss, aged 24 (Zürich Polytechnic and Ph.D.) thorough knowledge of English, French, and German, desires

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THE CHEMICAL NEWS.

Vol. XCVIII., No. 2552.

ELECTROSCOPIC DETERMINATION OF THE RADIUM PRESENT IN SOME "TUFA" DEPOSITS FROM HOT SPRINGS, ARKANSAS.*

By HERMAN SCHLUNDT.

The Hot Springs of Arkansas are situated in the central part of the State, on the western slope of a ridge known as Hot Springs Mountain. The thermal waters issue from fifty separate vents in the old and grey hot-spring deposit, or "tufa," that covers the lower slopes of the mountain of sandstone and shale (W. H. Weed, "Geological Sketch of the Hot Springs District, Arkansas." Senate Document, 1902, vol. xx., No. 282, 79. Government Printing Office, Washington, D.C.). The total flow is estimated at 850,000 gallons per day. The thermal waters at Hot Springs correspond closely to the ordinary springs of the surrounding mountain region, save in the one characteristic of temperature. They are regarded as entirely normal springs whose waters have been heated in the course of their underground flow by steam rising through fissures in the rock, the source of the heat being a hot, igneous mass of intrusive rock underlying this portion of the State.

In 1904, Dr. Boltwood, at the direction of the Secretary of the Interior, made a thorough examination of the waters of these springs for radio-active properties. (The results are summarised in a paper published by Dr. Boltwood in the *American Journal of Science*, 1905, xx., 128). In addition, samples of gases from two of the springs were examined; the residues from two samples of water were tested, and a sample of a spring deposit of "tufa" was included in the investigation. He tested all of the waters for radio-active gases—radium emanation—and a few of them for dissolved radium salts. Two water residues and one tufa deposit were tested for radium. The results of Dr. Boltwood's investigation showed that the waters possessed radio-activity, the activity being due to the presence of radium emanation. Two cold springs on the reservation were tested and also found relatively high in activity. No indication of radium salts in solution was obtained. The deposit of tufa examined was found practically free from radium; Dr. Boltwood states that the quantity of radium present in the tufa was less than one-millionth of the quantity of radium associated with an equal weight of uranium in pitchblende; or, in other words, the radium content of the tufa has the same order of magnitude as that found in an ordinary soil sample. One of the points of special interest that the results of Dr. Boltwood's investigation presented was the existence of marked variations in the activity of the different water samples, whose mineral constituents stand in such close resemblance. No connection could be established between chemical composition of the waters and the striking differences observed in their radio-active properties.

Elaborate chemical analyses of the waters of these springs have been made by Mr. J. K. Haywood, of the U.S. Dept. of Agriculture. The published results constitute the greater portion of Senate Document No. 282, *loc. cit.*

During the past year the writer has determined the quantity of radium present in several tufa deposits from Hot Springs. The results obtained demonstrate that the quantities of radium present in some of the samples examined greatly exceed the quantity found in the particular sample tested by Dr. Boltwood. Such marked variations as he found in the quantities of radium emanation present in the water samples are likewise exhibited by the tufa samples examined.

The specimens of tufa used for the tests were obtained through the courtesy of Mr. Martin A. Eisele, Superintendent of the Reservation (Mr. Eisele resigned the superintendency, April 1, 1907). He collected them during the past winter, and expressed them to Columbia, Mo., where the writer conducted the tests herewith described in the chemical laboratory of the University.

In determining the radium content of the deposits, the method devised by the Hon. R. J. Strutt in his investigations on the "Distribution of Radium in the Crust of the Earth" (*Proc. Roy. Soc.*, 1906, lxxvii., 472) was followed in the main. In this process the material to be tested must be converted into soluble form. As the tufa is calcareous in nature, digestion with hydrochloric acid dissolves most of the material. The principal steps of the operation are as follows:—An air-dry sample of about 200 grms. was pulverised and passed through an 80-mesh sieve. It was then dried for an hour at 105° C. A suitable quantity was then weighed out and dissolved in hydrochloric acid. When the insoluble residue exceeded 2 per cent, it was filtered off and rejected. Fusion of one of these residues with mixed carbonates of sodium and potassium and subsequent solution and treatment showed that it was practically free from radium. The solution or chlorides was then stored for several weeks in a tightly-corked flask of suitable capacity to permit the accumulation of the radium emanation produced by the radium salts in the solution. After a lapse of a month, when the accumulated emanation had reached a maximum, it was separated from the solution by boiling, the expelled gases being collected in a suitable reservoir. (For a description of the apparatus employed and the experimental details, the reader is referred to a former paper by Schlundt and Moore, *Journ. Phys. Chem.*, 1905, ix., 320). The gas was then transferred to a partially exhausted air-tight electroscope supplied with a reading microscope. From the rate of fall of the charged leaf, the quantity of radium required to produce the emanation in the electroscope, *i.e.*, the radium in the sample, was finally calculated.

The testing apparatus had previously been carefully standardised, by means of a known quantity of radium emanation obtained from a sample of uraninite whose uranium content was known. This method of standardising electroscopes was first proposed by Boltwood. It is based upon the well-established fact that the radium present in a natural mineral stands in constant ratio to the uranium it contains. The operation of standardising was carried out as follows: — A few mgrms. of a standard sample of uraninite were carefully weighed out, dissolved in dilute nitric acid in an apparatus that permitted the quantitative collection of the emanation. The emanation, mixed with other gases, was then introduced into the electroscope to be standardised, and the maximum rate of fall of the charged leaf determined. From these data a factor was computed for the instrument, expressing the quantity of uranium required to produce a fall of the charged leaf corresponding to one scale division per minute of the reading microscope. The uranium values for the activities were then cohverted into radium values by multiplying by the ratio of radium to uranium. The recent value of this ratio, as again determined by Rutherford and Boltwood, viz., $3{\cdot}8 \times 10^{-7}$, was employed in the calculations (*Am. Journ. Sci.*, 1906, xxii., 1).

The same sample of hydrochloric acid served for all the determinations. A blank test showed no indication of radium.

The quantitative results of the radium content of the tufa samples tested are given in the following table:—The first column gives the laboratory number, the second the weight of the sample taken for the determination, the third the percentage of insoluble residue, a "small" residue meaning less than 2 per cent. The last column gives the radium found per grm. of tufa, the radium unit being 1×10^{-12} grm.

* A Paper read by title at the Twelfth General Meeting of the American Electrochemical Society at New York City, October 18, 1907.

Table of Results.

Laboratory number.	Weight of sample taken (grms.).	Percentage of insoluble residue.	$g \times 10^{12}$ radium per grm of tufa.
1	152	Trace	0·72
2 A	175	Small	26·7
2 B (*a*)	125	Small	26·6
3	100	Small	2·62
4 A	120	6·7	2·32
4 B	98	6·9	2·85
5 A	2	9·4	1900
5 B	1	9·4	1927
5 C	2	—	227
5 D (*a*)	?	—	1322
6	160	Small	0·73
7	120	8·1	156·0
8	100	5·5	0·56
9	50	18·0	1·18
10	140	Small	36·3
11	100	7·8	0·01 ?
12 (*b*)	100	—	$< 0·38$

(*a*) I am indebted to Prof. Moore, of Butler College for this determination.

(*b*) Sample of tufa examined by Dr. Boltwood. The value given in the table was computed from the quoted statement introduced at the beginning of this paper.

Discussion of Results.

The most interesting feature of the results obtained is represented in the marked variations in radium content exhibited by the different tufa samples. No chemical analyses of the tufas examined were undertaken, but inasmuch as the physical properties of the specimens varied considerably, differences in composition doubtless exist, notwithstanding the fact that the dissolved mineral constituents carried by the water from different springs bear a close resemblance to one another. A few of the samples had a compact crystalline structure and resembled white marble; others were porous, consisting of a framework of travertine intermingled with earthy material, in which some of the higher oxides of manganese are probably present, as considerable chlorine was set free during the digestion with hydrochloric acid. No one physical characteristic or group of physical properties could be singled out, however, as representative of the more active samples. The specimens that left only small quantities of brown oxides when treated with cold hydrochloric acid of four-normal strength were found low in radium; but the presence of a relatively large quantity of insoluble material before the temperature of digestion was raised was found not to be a general accompaniment of high activity. Finally, a careful comparison of the mineral constituents of the spring waters that deposited the tufa of high radium content with those of low values fails to furnish any clue to the marked differences found in their radium content.

As stated before, marked variations in activity also characterise the water samples. Whether a parallelism exists between the content of radium emanation in the waters and the quantity in the tufa deposits cannot be stated, as Dr. Boltwood has designated his samples by laboratory numbers. The same system was followed in this paper upon suggestion of the Superintendent of the Reservation.

It is seen that the quantities of radium in Samples 1, 6, 8, and 9 are of the same order of magnitude as the radium content of the sample of tufa that came to Dr. Boltwood for examination, its maximum radium value being the last figure in the table of results.

Samples 2A and 2B are determinations on the same composite, as are also Samples 5A and 5B. In testing specimen No. 5, the calcareous crystalline material was partially separated and tested—5C; its activity was found to be only one-ninth the value obtained for the composite of the entire sample. It therefore appears probable that the radium occurs in pockets, and that it may be associated with some one of the different constituents of the tufa. Further investigations with a view of separating the radium-bearing constituents, either mechanically or by chemical means, would be of interest.

Another question for further investigation is suggested by the results:—Is the radium, found in these tufa deposits, in radio-active equilibrium with its parent, uranium? The quantities of uranium considered here are, in most of the samples, too small to be detected by chemical analysis; but in sample No. 5 the quantity of uranium would be sufficient for an analytical attempt. With 1900×10^{-12} grms. of radium there should be associated $1900 \times 10^{-12}/3·8 \times 10^{-7}$ grms. uranium, or 0·005 grm., *i.e.*, ½ per cent uranium. Unfortunately, in the course of the preliminary tests conducted with this interesting sample, most of it was lost, and up to the present time arrangements for securing more of the deposit have not been made.

Sample No. 11 does not properly belong in the table. This was a sample of loadstone probably deposited by hydrothermal action at Magnet Cove, Arkansas, an extinct locality of hot springs in this region.

The number of samples reported here represents but a small fraction, probably less than one-fifth of the deposits of tufa, but the results obtained are of sufficient interest to warrant a more complete investigation. An examination of the underlying sandstones and shales, and the dikes and igneous rock of the locality, would also be of interest in furnishing data as to the source of the radium in the spring deposits.

Discussion.

Prof. Schlundt (communicated):—Dr. Boltwood has kindly communicated the official numbers of the springs that correspond to the laboratory numbers in his paper (*loc. cit.*). This courtesy enables me to correlate the activities of the water and tufa samples. The data are summarised in the following table. The values for the activity of the water samples are expressed in grms. of uranium per litre of water, as in Dr. Boltwood's paper. The official numbers of tufa Samples 1 and 2 are in doubt, and are therefore not included in the table. Samples Nos. 8 and 9 were tufas taken from caves for which corresponding water samples were not treated.

Laboratory number of tufa sample.	Activity of tufa; $g \times 10^{-12}$ radium per grm. of tufa.	Activity of water; $g \times 10^{-4}$ uranium per litre of water.
3	2·62	5·3
4	2·65	12·9
5	1900	3·4
6	0·73	3·7
7	150	26·1
10	36·3	22·0
12	0·38	41·6

The limited number of results thus correlated—there are fifty springs—indicate that a correspondence between content or radium emanation in the waters and radium present in the tufa deposited by the waters does not exist.

SOME CHARACTERISTIC COLOUR REACTIONS PRODUCED BY SODIUM HYPOBROMITE.

By WILLIAM M. DEHN and SILAS F. SCOTT.

Since hippuric acid gave with sodium hypobromite a very characteristic colour reaction, it was thought that other substances also would be affected characteristically by this reagent (see *Journ. Am. Chem. Soc.*, xxx., p. 1507; Chemical News, vol. xcviii., p. 181). This has proved to be the case and to such an extent that sodium hypobromite alone or combined with the use of ammonia can now be considered one of the most valuable reagents for detecting and distinguishing many phenolic and nitrogenous aromatic compounds.

For the purpose of uniformity and of determining the

limits of tests and comparing their respective delicacies, solutions of the various substances were prepared in the following concentrations:—I., 1 grm. in 100 cc. of water; II., in 1000; III., in 10,000; IV., in 100,000; V., in 1,000,000.

Alcohol was added when necessary to produce complete solution; with bases, hydrochloric acid was used for the same purpose. With various concentrations of solutions quite different colour effects may often be obtained, and thus one sometimes obtains results quite different from the results described in the literature. For this reason the concentrations of solution should always be indicated, also the quantity used, method of applying the reagent, quantity of reagent, and the temperature. In the following experiments the reagent was applied, a drop at a time, to about 5 cc. of the solutions tested. When a series of colours are given they indicate the progressive effect either on standing or on adding more of the hypobromite solution. The following abbreviations are used to indicate the conditions and manner of applying tests:—

(A). Treated with sodium hypobromite at ordinary temperature.
(A′). Treated with ammonia, then with sodium hypobromite at ordinary temperature.
(B). First heated to boiling, then treated with sodium hypobromite.
(B′). Treated with ammonia, then heated and finally treated with sodium hypobromite.

Of course solutions should not be acid in reaction, for then bromine is liberated from the hypobromite. Excess of ammonia should be avoided for the reason that it destroys the hypobromite. Care should be exercised that the hypobromite is added gradually, for the reasons not only that often a series of colours may thereby be developed but that the possible destruction of colour by an excess of hypobromite may be avoided. Conditions of experiments and concentrations of solutions yielding negative results are omitted in the following descriptions. When heat and the addition of ammonia give effects that are the same as (A), only the effects of the latter are described.

Phenolic Compounds.

*Phenol.**—(B) and (B′): I., deep chrome-green; II., same; III., light sea-green. Ammonia is necessary, and heat assists this colour reaction.

Pyrocatechinol.—(A), (A′), (B), (B′): I., II., bright green followed immediately by a deep brown. (B). (B′): III., pink-brown followed by amber-brown. Most sensitive with ammonia and heat. Colour is changed to yellow by an excess of sodium hypobromite.

Resorcinol.—(A): I., bromine-brown; II., amber-brown; III., straw-yellow. (A′): I., deep brown-black; II., deep amber-green. (B): I., amber-brown; II., amber-green; III., green-amber; IV., straw-yellow. (B′): I., deep brown-black; II., deep amber-green; III., green-amber; IV., faint pink. Colour is intensified by the use of ammonia and heat; destroyed by an excess of sodium hypobromite and continued heat.

Hydroquinol—(A): I., chrome-green, changing immediately through bromine-brown to deep brown-black; II., chrome-green to deep brown; III., transient light green. (A′): I., deep brown; II., same; III., very transient light green. (B): Ammonia itself imparts a golden-amber hue; I., dark brown; II., deep amber; III., light amber. Less sensitive with ammonia and heat; an excess of sodium hypobromite discharges the colour, yielding odour resembling quinone.

To Distinguish the Dihydric Phenols.—To about 0·1 per cent solution of each add one drop of ammonia; hydroquinol gives a golden-yellow colour. Add 2—3 drops of sodium hypobromite; pyrocatechinol gives a dark brown, resorcinol gives a green, and hydroquinol gives a brown-red colour.

Pyrogallol.—(A): I., amber, brown-red, deep black-brown; II., amber, deep brown-red; III., amber. (A′): Same as (A) but less sensitive. (B): Ammonia alone imparts an amber colour; I.—III., same as above. IV., amber.

Phloroglucinol.—(A): I., green-amber, green-brown, deep violet, deep violet-brown; II., violet, red-brown, amber. (A′): I., black-brown; II., brown-red. (B) and (B′): I., deep violet, deep brown-black; II., deep violet; III., violet. The violet colour, best formed with ammonia in a warm solution, easily distinguishes phloroglucinol from the other phenols.

Orthocresol.—(A): I., dirty chrome-green, brown, dirty brown; II., brown-amber, brown. (B): I., Paris green, deep black-green, dirty green, yellowish precipitate; II., brilliant chrome-green, grass-green, amber; III., sea-green, straw-yellow.

Metacresol.—(A): I., pink-amber, light-brown; II., amber. (B): I., blue-green, deep black-green, brown, amber, dirty white precipitate; II., brilliant emerald-green, green-amber, amber; III., light green, amber.

Paracresol.—(A): I., pink, pink-amber, light brown, dirty white precipitate; II., pink, amber; III., light yellow. (B): I., light amber, brown; II., amber.

The cresols are distinguished by the lack of formation of a green colour with the para, when treated with ammonia and sodium hypobromite; the ortho forms a dark brown, the meta a light brown, when treated with sodium hypobromite.

"*Cresol.*"—(A): I., pink, wine-red, deep brown-red; II., amber, pink, amber, red, brown; III., light yellow. (B): I., sea-green, deep dirty green, deep brown; II., light pink-amber, amber-brown; III., amber.

α-Naphthol.—(A): I., purple, purple-black, brown-black; II., purple, dirty green-black, green-brown, purple-violet; III., sea-green, amber, pink-violet; IV., faintly pink. (A′): I., dirty green, brown, black-brown, brown-black; II., sea-green, brown-amber; III., yellow-green. (B): I., blue-green, indigo-blue, green-black; II., blue-green, dirty green. (B′): I., dirty green, deep brown; II., sea-green, dark amber-brown.

β-Naphthol.—(A): I., yellow-green, dark amber-brown, brown-black; II., green-amber, deep brown; III., amber; IV., straw-yellow. (A′): I., pink-brown, wine-red, deep red-brown; II., pink-amber, red-brown; III., pink-amber. (B): I., amber, yellow-green, green-brown; II., amber, brown-amber. *The naphthols are distinguished* best in (A) II. solutions; purple with the *α*, brown with the *β*.

Derivatives of Phenols.

Salicylic Acid.—(B), (B′): I., II., light chrome-green. Colour changed to amber by an excess of sodium hypobromite, restored to green by the addition of more ammonia.

Thymol, 2-isopropyl-5-methylphenol. (B′): I., II., brilliant nickel-green; III., faintly green colour. Excess of ammonia is to be avoided. This is a very beautiful and characteristic test for thymol.

Salol.—(B′): I., same as phenol and salicylic acid. Colour develops best after heating and standing.

Guaiacol, *o*-methoxyphenol. (A), (A′): I., deep red-brown; II., amber-brown. (B), (B′): I., deep blue-green or black-green; II., chrome-green. The colours of guaiacol resemble the colours of phenol more closely than of pyrocatechol.

Vanillin, 3-methoxy-4-oxybenzaldehyde. (B′): I., II., beautiful amber colour.

Arbutin.—(A): I., pink, amber; II., same. (B): I., deep nickel-green; II., same.

Eugenol, 4-propenyl-2-methoxyphenol.—(A), (A′), (B), (B′): I., II., golden yellow, changing to deep brown.

Oil of Bay, contains eugenol. (B′): I., clear deep red-brown; II., brown-yellow. Ammonia alone gives a bright lemon-yellow.

Oil of pimento, contains eugenol. (B′): I., red-amber, brown, deep red-brown; II., red-amber, brown, amber. Ammonia alone gives a bright lemon-yellow.

* A blue colour with bleaching powder is described: Lex, *Ber.*, iii., 458; Salkowski, *Zeit. Anal. Chem.*, xi., 316; *Jsb. Chem.*, 1873, 722.

Scores of other fixed and volatile oils, tested as described above, failed to give characteristic colour tests. Homogeneous aromatic oils like safrol, apiol, and anethol failed to give the colour tests even after boiling for some time with concentrated alkalis. Under these conditions oil of winter-green gave the same green colour as salicylic acid.

Gallic Acid.—(A): I., pink, amber, brown, black-brown; II., pink, pink-amber, grass-green, amber-green, brown, amber; III., pink, brown, amber. Alkalis alone give first a pink, then a grass-green, and finally a brown colour, but the action is greatly quickened and intensified by means of sodium hypobromite.

Tannic Acid.—(A): I., II., pink, amber, brown, deep brown; III., pink, pink-amber, amber; IV., pink. Alkalis alone give first a pink, then a brown colour; here as with gallic acid, owing to the oxidising power of the hypobromite, the action is greatly quickened and intensified.

Aromatic Nitrogen Compounds.

Aniline.—(A): I., orange-red, deep red-brown; II., smoky amber, deep orange; III., amber, dirty orange; IV., light yellow. (A′): I., orange, deep brown; II., orange, deep brown; III., amber. With (A′) I. solutions, odour of phenylisocyanide.

o-Toluidine.—(A): I., brick-red, violet, purple, purple-black, deep brown-black; II., brown-red or orange-red; III., red-amber; IV., light straw-yellow. (A′): I., violet, purple, purple-black; II., yellow, pink-amber, brown-red; III., golden yellow. With (A′) I. solutions, odour of phenylisocyanide.

p-Toluidine.—(A): I., pink, rose-red, red-brown; II., pink, dirty yellow. (A′): I., violet, dark brown; II., pink-amber, golden brown.

These two toluidines and aniline are easily distinguished by the orange colour with aniline and by the changes of colour and deeper colours of *o*-toluidine.

p-Phenylenediamine.—(A): I., bright blue-green, deep purple, black-purple, brown-black; II., deep grass-green, deep purple, dirty brown; III., grass-green, amber-brown, violet-purple, curdy white precipitate; IV., bright amber. (A′): I., dark blood-red, purple, brown-black; II., deep brown-red; III., amber. (B′): I., II., deep purple, brown; III., brown amber. Very characteristic colour effects.

m-Nitraniline.—(A): I., yellow, dirty brown; II., ochre-yellow; III., light yellow. (A′): I., red-brown; II., dirty brown; III., light yellow.

p-Sulphanilic Acid.—(B′): I., deep red-brown; II., amber; III., light yellow.

Benzamide.—(A′): I., II., yellow, deep brown, brown-black, precipitate; III., amber-yellow. The colour is not easily discharged by an excess of hypobromite. An intense odour of phenylisocyanide is given off.

Phenylurethane.—(A′): I., brown or brown-red colour, odour of phenylisocyanide; II., cloudy yellow. (B′): I., orange, brown.

Phenylhydrazine.—(A′): I., II., dirty orange.

Ammonol, ammonia-phenylacetamide. (B′): I., yellow-red coloured precipitate; II., amber.

Fatty amides and amines fail to yield colour effects with sodium hypobromite, in fact no *aliphatic* compound responds to this reagent. It is specifically an *aromatic* test reagent.

Alkaloids.

Some forty of the most common alkaloids and glucosides were tested with sodium hypobromite; only the following ones gave definite colour reactions.

Morphine.—(A′), (B′): I., deep amber-brown; II., amber; III., light yellow. The test is best made with the use of ammonia; the colour is discharged by an excess of hypobromite.

Codeine and Dionine gave the same as morphine, only less sensitive.

Apomorphine.—(A): I., deep brown, deep chrome-green; II., pink-amber, deep brown, deep chrome-green, lighter green, amber; III., light pink, light yellow. This is a very characteristic reaction, particularly in solution II.

*Physostigmine or Eserine.**—(A): I., light red; II., pink. (A′): I., deep blood-red; II., bright bichromate-red; III., rose-pink. Alkalis give a red colour, but the hypobromite with heat deeply intensifies the red.

Antipyrine.—(A): I., pink-amber. Colour discharged by an excess of hypobromite.

Phenacetine.—(B′): I., deep amber-brown; II., amber.

Acetphenetidine.—(B): I., deep amber-brown; II., amber.

Though not giving characteristic colour effects, some of the other alkaloids gave off characteristic odours. For instance, scopolamine and hyoscyamine gave a phenylisocyanide-like odour, caffeine a methylamine odour, and atropine and cinchonidine other characteristic odours. From consideration of the above-described colour reactions and negative results obtained with scores of other organic groups, it is concluded that hypobromite is an invaluable reagent for detecting and distinguishing phenolic and aromatic amino compounds. None of the aliphatic or terpene compounds tested gave colour effects; only compounds of the types :—

$$>OH \qquad >NH_2 \qquad >CONH_2.$$

With *p*-phenylenediamine, it yields nearly quantitatively a white crystalline solid melting with decomposition at 105°. This and other products of the hypobromite reaction are being investigated.—*Journal of the American Chemical Society*, xxx., No. 9.

THE ELECTROLYTIC DETERMINATION OF BISMUTH.

By F. J. METZGER and H. T. BEANS.

Much has been written about the determination of bismuth in the electrolytic way and many electrolytes have been proposed. Without attempting any detailed discussion of the numerous publications which have appeared on the subject, the difficulties with which one almost invariably has to contend may be briefly summed up as follows :—

When a bismuth solution is electrolysed there is deposited not only metallic bismuth on the cathode, but frequently there is a simultaneous deposition of peroxide on the anode, and it has been suggested that both anode and cathode be weighed for each determination. Again, the deposited metal is nearly always black and spongy, and in cases where accurate results have been obtained it has been necessary to exercise the greatest care in washing and drying in order to prevent loss mechanically. A method which has been recommended especially for comparatively large quantities of bismuth is the amalgam method originally proposed by Vortman (*Ber.*, xxiv., 2749). In this method a known quantity of mercury salt is added to the bath and the deposit of bismuth amalgam weighed. From this weight the bismuth is obtained by difference. The quantity of mercury recommended is four times that of the bismuth present.

The method described in this paper presents none of the difficulties encountered in previous methods; the metal is deposited in compact, adherent form and can be washed and dried without any possible chance of loss, nor is there ever any deposition of peroxide on the anode when the electrolysis is completed.

It has been found that by the addition of acetic acid to a bismuth nitrate solution precipitation by hydrolysis may be completely prevented, even though the solution be subsequently largely diluted. It is also possible to obtain this result by first eliminating all free nitric acid by the addition of sodium hydroxide to alkaline reaction and then

* With bleaching powder, an intensely red colour; Eber, *Zeit. Anal. Chem.*, xxviii., 134; Ferreira, *Bl.* [3], ix., 753.

Table I.

Expt. No.	50 per cent acetic acid.	Boric acid.	Volume.	N.D.$_{10}$ (*a*).	Voltage.	Temperature.	Time.		Bi taken.	Bi found.	Error.
	Cc.	Grms.	Cc.				Hrs.	Mins.			
1.	20	2	250	0·2—0·15	2·1—2·8	74—79°	0	45	0·03956	0·0391	− 0·00046
2.	20	2	250	0·2—0·175	1·9—2·75	75—79	1	15	0·0989	0·0990	+0·0001
3.	20	2	250	0·2—0·15	1·9—2·8	72—75	1	30	0·0989	0·0990	+0·0001
4.	20	2	250	0·2—0·17	1·9—2·75	63—77	1	15	0·0989	0·0989	—
5.	20	None	250	0·2—0·15	1·9—2·7	74—78	1	15	0·0989	0·0989	—
6.	20	2	250	0·2—0·15	1·9—2·65	74—83	1	15	0·0989	0·0987	− 0·0002
7.	20	2	250	0·2—0·15	1·85—2·74	72—77	1	15	0·0989	0·0989	—
8.	20	None	250	0·2—0·125	1·8—2·6	77—79	1	15	0·0989	0·0986	−0·0003
9.	20	2	250	0·2—0·2 (*b*)	1·9—2·8	75—78	1	15	0·0989	0·0984	− 0·0005
10.	20	2	250	0·2—0·17	1·85—2·75	76—78	1	15	0·0989	0·0992	+0·0003
11.	20	2	250	0·2—0·17	1·8—2·72	76—79	1	15	0·0989	0·0992	+0·0003
12.	20	2	250	0·2—0·17	1·8—2·64	77—88	1	15	0·0989	0·0991	+0·0002
13.	20	None	250	0·2—0·175	1·8—2·4	75—78	1	15	0·0989	0·0990	+0·0001
14.	20	2	250	0·2—0·175	1·8—2·7	73—77	1	15	0·1978	0·1981	+ 0·0003
15.	20	2	250	0·2—0·16	1·8—2·6	76—77	1	15	0·1978	0·1979	+0·0001
16.	20	2	250	0·2—0·16	1·8—2·55	73—78	1	15	0·1978	0·1978	—
17.	20	2	250	0·2—0·17	1·77—2·55	70—80	1	15	0·1978	0·1980	+0·0002
18.	20	None	250	0·2—0·175	1·75—2·37	75—81	1	20	0·1978	0·1984	+ 0·0006
19.	30	None	250	0·2—0·16	1·8—2·45	70—78	2	15	0·3956	0·3962	+0·0006
20.	30	2	250	0·2—0·175	1·75—2·5	70—78	2	15	0·3956	0·3953	− 0·0003
21.	30	None	250	0·2—0·15	1·7—2·42	73—79	3	15	0·3956	0·3955	−0·0001
22.	30	2	250	0·2—0·16	1·75—2·55	74—77	2	15	0·3956	0·3956	—
23.	30	2	250	0·2—0·175	1·72—2·45	74—79	2	15	0·3956	0·3957	+ 0·0001
24.	30	2	250	0·2—0·175	1·75—2·50	78—79	2	20	0·3969	0·3968	− 0·0001
25.	30	None	250	0·2—0·175	1·76—2·55	75—80	3	30	0·3969	0·3969	—
				N.D.$_{100}$.							
26.	30	2	350	0·5—0·17	1·9—2·5	78—80	1	30	0·3969	0·3972	+0·0003

(*a*) The figures in the second column represent the point to which the current drops at the end of the experiment.
(*b*) In this experiment the current was maintained constant.

re-dissolving the precipitated bismuth hydroxide by means of acetic acid, the whole operation being carried out in the cold. It has also been observed that the addition of boric acid to the bath has a decided effect on the character of the deposit, and in addition it serves to bring about, readily, complete solution of bismuth hydroxide without the addition of very large quantities of acetic acid.

The apparatus employed is a slightly modified form of that originally proposed by Gooch and Medway (*Am. Journ. Sci.*, [4], xv., 320), using a rotating cathode. The platinum thimble employed as cathode was connected to the shaft by means of a rubber stopper wound with fine platinum wire for contact, and had an available surface of forty square centimetres. In all cases it was driven at the rate of about seven hundred revolutions per minute.

As a basis for the experiments a bismuth solution was prepared by dissolving chemically pure bismuth nitrate in water containing 25 cc. conc. nitric acid per litre. The solution was then carefully standardised by gravimetric methods.

The method of procedure was in all cases as follows:—To a known quantity of the standard solution phenolphthalein was added, then sodium hydroxide solution, drop by drop, to alkaline reaction. The precipitate formed was re-dissolved in acetic acid and then 2 grms. of boric acid were introduced. The solution was diluted, heated to 70° to 80°, and electrolysed. The working conditions are shown in Table I.

In Experiments 19 to 25 inclusive, the amount of acetic acid given does not completely re-dissolve the precipitate, but after the addition of the boric acid the solution becomes perfectly clear. In Experiments 19, 21, and 25, in which no boric acid was used, the slightly opalescent solution was electrolysed, the solution, however, becoming perfectly clear during the period of the electrolysis.

The change in voltage during the electrolysis serves as an excellent indicator in the determination. The voltage remains constant until all but the last trace of bismuth has been deposited, when it begins to rise rapidly to a maximum at which it again remains constant. The electrolysis should be continued five or ten minutes beyond this maximum point. In Table I. the voltages recorded show the initial and final values. Table II. being a record of Experiment 16 makes this a little more clear.

Table II.

Time, p.m.	N.D.$_{40}$.	Voltage.	Temperature.
2.50	0·2	1·8	73°
3.05	0·2	1.8	75°
3.20	0·2	1·8	76°
3.35	0·2	1·8	78°
3.43	0·19	2·0	78°
3.45	0·18	2·1	78°
3.50	0·175	2·4	78°
3.55	0·175	2·5	78°
4.00	0·160	2·55	78°
4.05	0·160	2·55	78°

The action of acetic acid on the deposited metal was found to be so slow that it is not necessary to syphon off the liquid at the end of the experiment. All that is required is to quickly substitute a beaker of water without interrupting either the current or rotator. The thimble is then detached, washed with alcohol and ether, allowed to dry, and weighed after standing on the balance for ten minutes. To avoid any errors which might arise from changes in atmospheric conditions, the weight of the thimble was taken after dissolving off the deposited metal by immersing in nitric acid, washing and drying, &c., the same as above.

In all of the experiments given in Table I. the available cathode surface was forty square centimetres, and it was naturally supposed that a stronger current could be employed with a larger electrode, and in this way the time factor might be reduced. A larger electrode having an available surface of one hundred square centimetres of the same form as the one previously used was procured with which we obtained the result shown in Experiment 26.

In working with this larger electrode the current should be reduced to 0·2 ampère at the time whe
begins to rise.

As seen in the table the results are accurate without the use of boric acid. The metal is deposited in bright, compact form up to the time when the voltage begins to rise, *i.e.*, when only very small quantities remain in solution. From this point, if there be no boric acid present, the last traces of metal deposit over the surface of the bright coating in the form of a granular layer less firmly adherent and somewhat darker. With boric acid present the deposition is uniform to the very end of the experiment, giving a mooth, compact, adherent deposit having the characteristic colour of the metal.

In not a single experiment was there any evidence of peroxide formation on the anode at the close of the determination. Occasionally there was a slight tinge of yellow on the anode at the very beginning of the electrolysis, but this, however, soon disappeared. The solution after each determination was examined for bismuth and none could be found.

The effect of boric acid on the deposition of other metals is being studied.—*Journal of the American Chemical Society*, xxx., No. 4.

FIFTEENTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUBLISHED DURING 1907.*

By F. W. CLARKE.

(Concluded from p. 193).

Tellurium.

THE research upon tellurium, by Baker and Bennett (*Journ. Chem. Soc.*, xci., 1849), was primarily to determine the homogeneity of the element. Various fractionating processes were employed, but tellurium of the same atomic weight was produced in every case. Two methods, both new, were adopted for the atomic weight determinations. First, TeO_2 was heated with sulphur in tubes of glass, the two ends of the tube being packed with pure silver leaf. Sulphur dioxide was expelled, and from its amount, as measured by the loss of weight, the percentage of oxygen in the TeO_2 was computed. For this purpose the value S = 32·06 was assumed. The determinations by this method fall into three principal series, as follows, representing differences in the source of the initial substance:—1. Fractional crystallisation of telluric acid from barium tellurate. 2. Fractional crystallisation of telluric acid from oxidation of the element. 3. Tellurium dioxide prepared from tellurium hydride. Vacuum weights are given throughout. The data are as follows:—

Fraction.	Weight TeO_2.	Loss SO_2.	Per cent O in TeO_2.
	SERIES 1.		
1.	1·51509	0·60838	20·055
2.	1·09875	0·44074	20·034
3.	1·02150	0·40993	20·046
4.	0·90835	0·36472	20·053
5.	1·00702	0·40451	20·062
6.	1·01515	0·40733	20·044
	SERIES 2.		
1.	1·56837	0·62938	20·046
2.	1·07852	0·43257	20·035
3.	1·72627	0·69296	20·052
4.	2·09253	0·83927	20·032
5.	0·83335	0·33465	20·059
6.	1·15372	0·46284	20·041
7.	1·68618	0·67661	20·045
8.	0·90835	0·36472	20·053
	SERIES 3.		
1.	1·02217	0·41050	20·064
2.	0·80697	0·32322	20·051
3.	1·32003	0·52992	20·053
4.	1·05207	0·42221	20·047
5.	1·37043	0·54969	20·032
6.	0·95944	0·38511	20·048

* From the *Journal of the American Chemical Society*, xxx., No. 3.

Several other experiments, concordant with these, are cited, but without the detailed weighings.

The other method employed consisted in converting tellurium into the tetrabromide by direct union with bromine in an atmosphere of nitrogen. Here, again, several series of determinations are given. For brevity, the data are combined in one table:—

Series.	Weight Te.	Weight $TeBr_4$.	Per cent Te.
1.	0·61273	2·14933	28·508
	0·56866	1·99354	28·525
	0·59884	2·09951	28·523
	0·57894	2·03040	28·514
	0·54743	1·91899	28·527
	0·33859	1·18732	28·517
	0·56866	1·99354	28·526
	0·47643	1·67025	28·525
	0·56622	1·98597	28·511
2.	0·44271	1·55205	28·524
	0·41671	1·46177	28·508
	0·50611	1·77489	28·515
3.	0·37382	1·31081	28·519
	0·31895	1·11868	28·512
	0·48931	1·71554	28·522
	0·47156	1·65404	28·510
4.	0·40748	1·42867	28·523
	0·62013	2·17449	28·518
5.	0·37382	1·31081	28·519
	0·50822	1·78207	28·518
	0·12928	0·45354	28·505
	0·42926	1·50540	28·515
6.	0·80348	2·81715	28·511
	0·95309	3·34193	28·512

From the dioxide determinations, the authors compute that Te = 127·609. From the bromide syntheses, if Br = 79·96, Te = 127·601. They also give, but without details, several determinations based upon analyses of tellurium tetrachloride. Four fractions of the chloride gave for Te the values 127·58, 127·60, 127·64, 127·62. The commonly accepted value, 127·6, thus receives strong confirmation.

On the other hand, quite different results have been announced by Marckwald (*Ber.*, xl., 4730). He prepared pure telluric acid, H_6TeO_6, which, by heating under proper precautions, was reduced to TeO_2. His figures, on the basis of O = 16 and H = 1·008, are subjoined.

Weight acid.	Weight TeO_2.	At. wt. Te.
8·6277	5·9884	126·93
12·2680	8·5135	126·84
13·0051	9·0244	126·80
8·6415	5·9947	126·65
8·4588	5·8696	126·80
8·0113	5·5599	126·94
	Mean, excluding No. 4 ..	126·86

From the sums of the weights Marckwald, rejecting the fourth determination, computes Te = 126·85. This falls below the atomic weight of iodine, and is in harmony with the periodic law. Since, however, it diverges so widely from many, concordant, higher determinations, it evidently needs corroboration by other experimenters and other methods.

Ytterbium and Lutecium.

According to Urbain, ytterbium is a mixture of two elements, neo-ytterbium and lutecium (*Comptes Rendus*, cxlv., 759). The atomic weight of neo-ytterbium is not far from 170; that of lutecium is perhaps a little above 174. Detailed determinations are yet to be made. In a footnote Urbain remarks that the atomic weight of thulium, which is given as 171 in the tables, is certainly below 168·5.

Radium.

Madame Curie has re-determined the atomic weight of radium, with purer material than that used in her former researches, and in larger quantities (*Comptes Rendus*, cxlv., 422). The well known chloride method was employed, with the subjoined results :—

Weight $RaCl_2$.	Weight Ag Cl (*a*).	At. wt. Ra.
0·4052	0·3906	226·35
0·4020	0·3879	226·04
0·39335	0·3795	226·15
	Mean	226·18

(*a*) From the weights of AgCl, 0·00006 grm. is to be deducted in each case, representing filter ash.

Calculated with Ag = 107·8 and Cl = 35·4. With Ag = 107·93 and Cl = 35·45, Ra becomes 226·45, or 226·5 in round numbers. It is announced that Thorpe is also engaged upon a re-determination of this constant.

Gaseous Densities.

Gray (*Proc. Chem. Soc.*, xxiii., 119) has determined the density of gaseous hydrochloric acid, and assigns to the weight of 1 litre, under standard conditions and in latitude 45°, the value 1·6397 grms.

Guye (*Comptes Rendus*, cxlv., 1164) has discussed the data relative to nitrogen and some of its gaseous compounds, and assigns to it the atomic weight 14·010. D. Berthelot (*Comptes Rendus*, cxlv., 65), from essentially the same data finds N = 14·005. In an elaborate discussion of the whole subject, Guye has finally adopted the following figures for the weight in grms. of 1 litre of each gas considered. (See *Arch. Sci. Phys. Nat.*, [4], xxiv., 34; *Journ. Chim. Phys.*, v., 203; *Comptes Rendus*, cxliv., 976; CHEMICAL NEWS, xcvi., 175; *Journ. Am. Chem. Soc.*, xxx., 143. Other papers, mostly controversial, are as follows: Guye, *Comptes Rendus*, cxliv., 1360; Berthelot, *Ibid.*, cxliv., 76, 269) :—

O_2	1·42900	N_2O ..	1·9777
H_2	0·08987	HCl . ..	1·6398
N_2	1·2507	NH_3 ..	0·7708
CO	1·1504	SO_2 . ..	2·9266
NO . ..	1·3402	Air	1·2928
CO_2 . ..	1·9768		

Miscellaneous Notes.

Watson (*Nature*, lxxvii., 7), in a brief note, has considered the simultaneous calculation of atomic weights from a group of related ratios. Hinrichs (*Comptes Rendus*, cxlv., 715) has proposed a graphic method for achieving the same purpose. He has also published several papers in which he seeks to establish integral values for the atomic weights of Br, Mn, and Cl (*Comptes Rendus*, cxliv., 973, 1343; cxlv., 58; see also *Chem. Zentralb.*, 1907, p. 1958).

A number of writers have discussed relations between the atomic weights. (See Wilde, *Manchester Lit. Phil. Soc.*, li., [1], No. 2; Stromeyer, *Ibid.*, No. 6; Minet, *Comptes Rendus*, cxliv., 428; Collins, CHEMICAL NEWS, xcvi., 176; Verschoyle, *Ibid.*, xcvi., 197; Delauny, *Comptes Rendus*, cxlv., 1279). On the question of standards, see Erdmann (*Chem. Zeit.*, xxxi., 95), and especially Swarts (*Bull. Acad. Roy. Belg.*, Classe des Sciences, 1907, No. 3, p. 212). The latter proposes two methods by which the atomic weights may be connected with the gas equation and with the absolute system of units. General papers on the subject of atomic weights are by Brauner (*Chem. Zeit.*, xxxi., 483) and Richards (*Ber.*, xl., 2767). Richards's paper is in the form of a lecture delivered before the German Chemical Society.

Lectures on Milk.—Dr. Harden, of the Lister Institute of Preventive Medicine, will give a course of Six Lectures on "Milk," at the South-Western Polytechnic, on Thursday evenings, commencing October 29, at 8 p.m. Each lecture will be illustrated by specimens and lantern slides and will appeal to managers and others interested in the distribution of milk.

THE INFLUENCE OF FINE GRINDING ON THE WATER AND FERROUS-IRON CONTENT OF MINERALS AND ROCKS.*

By W. F. HILLEBRAND.

IT has been the general practice, following the directions of numerous writers, to reduce most rock and mineral powders to a very fine state of division preliminary to their analysis. This seemed called for on several grounds—to secure a proper sample of an inhomogeneous mixture, the need of extreme fineness for the ferrous iron determination, for that of the alkalis by the J. Lawrence Smith method, for all decompositions that involve the use of boric oxide or lead oxide, and in general in order to insure complete and speedy decomposition by fusion with an alkali carbonate. A very fine powder is, however, far less needed for the last-named purpose than has been commonly supposed. The writer's recommendation has been to prepare a main sample of moderate fineness and to grind separate small portions of this finer when needed.

Now comes the Swedish chemist, Robert Mauzelius, and shows that fine grinding is highly detrimental in the case of minerals containing ferrous iron because of its resulting oxidation (*Sveriges Geol. Undersökning Arsbok*, 1907, i., No. 3). Led by Mauzelius's work, Nicholas Knight has shown that siderite oxidises when finely ground (CHEMICAL NEWS, xcvii., 122). A. L. Day and E. T. Allen had shown how very great is the effect of fine grinding on the moisture content of minerals (*Pub. Carnegie Inst.*, No. 31, p. 56; *Am. Journ. Sci.*, xix., 93; *Bull. U. S. Geol. Survey*, cccv., 55); and Mauzelius in the paper cited adds to our knowledge on this point by quantitative data with respect to rock powders. These writers clearly show that coarse powders entirely free from hygroscopic water, or containing but a few hundredths of 1 per cent of it, take up moisture progressively as the grinding continues, and that the amount so taken up can readily be brought to exceed 1 per cent of the weight of the sample. This is, so far as amorphous minerals are concerned, entirely in harmony with what Bunsen observed for spun glass (*Wied. Ann.*, 1885, xxiv., 327), a condition in which the surface exposure is very great. Since many minerals and nearly all rocks contain ferrous iron, Mauzelius rightly insists that the determination of this component shall be made on the coarsest material that can be completely decomposed by the acid that is employed. Further, in view of the great absorption of atmospheric moisture, and in such varying degree according to the fineness of the sample that no two analysts can be expected to prepare samples of the same mineral that will contain like amounts of moisture, he argues that the old practice of stating the analysis in terms of dried material should be followed in preference to the later practice of reporting the moisture given off below 100—110° as well as that firmly held at that point. To this last recommendation objection may be made, as I shall show later.

The oxidation of ferrous iron was such an important observation in view of the extent to which it may go (up to about 40 per cent of the FeO present in one of Mauzelius's experiments) that the subject seemed to demand further investigation. It was evident that acceptance of the direction to use only relatively coarse powders would introduce serious complications and uncertainties into the execution of an analysis, for there are many minerals that cannot be readily decomposed by boiling hydrofluoric acid even when reduced to pass a sieve of 150 meshes to the linear inch (nearly 60 to the centimetre, or approximately 0·08 mm. width of apertures between wires). It was therefore necessary to devise, if possible, some means of fine grinding that would not involve oxidation of iron.

Much of the tabulated matter of this paper is but a confirmation and extension of what Allen, Day, and Mauzelius have shown, but its presentation in detail seems justified

* From the *Journal of the American Chemical Society*, xxx., No. 7.

on account of the intimate bearing of the subject on mineral analysis and its consequent importance to all mineral analysts, mineralogists, and petrologists. Often valuable observations have passed unheeded or insufficiently heeded, and been eventually forgotten. Frequent reiteration is called for if they are to become generally known and appreciated.

In the course of the experiments that were made on powders ground in air, no explanation that occurred seemed adequate to fully account for the oxidation of ferrous iron except that of strong local heating of the grains at the moment of fracture or attrition under the pestle. The effect should be especially marked with pyritic minerals. The idea of intense local heating, though at first thought improbable, becomes less so when it is remembered that steel strikes sparks from flint. If the oxidation is due simply to greater surface exposure it ought seemingly to continue at a lessened rate after cessation of the grinding, but powders finely ground in past years show to-day the same FeO content as when originally analysed. Of course, there is no general heating to account for the phenomenon, as when a rock is pulverised in a closed ball mill, where the temperature may rise to such a degree as to dehydrate the gypsum that is added to Portland cement clinker (see Note 1).

Led by the thought of local heating as the chief cause of oxidation of the ferrous iron, it occurred to me to test the effect of grinding on the content of water that is given off above 100—110°, and is supposed to be chemically held in large part, for it seemed possible that this might be reduced by grinding. If so, however, the loss is more than offset by a very large gain due to increased surface exposure, as the results tabulated below plainly show. This gain in firmly held water, quite in accord again with what might be expected in view of the firmness with which Bunsen found (*loc. cit.*) the adsorbed water to be held by glass, has an important bearing on the question of the permissible size of grain of a sample that is to be analysed, and strengthens in the strongest manner the argument of Mauzelius for a coarse sample. For the rock powders tested by myself, the increase in this firmly held water seems to be, as a rule, of nearly the same general order of magnitude as that of the loosely held moisture, but it is very much greater with the meerschaum tested (16 below).

The following remarks explain certain features of the table. The determinations of the first three numbers were made simply to test the claims of Mauzelius, those that follow relate also to increase of water above 105° under different conditions of grinding. The designations <100-mesh, <150-mesh (see Note 2), &c., mean that all the material was simply crushed to pass the respective sieves with as little production of fine powder as possible and without grinding. This was effected by brief crushing in the steel mortar figured on p. 46 of *Bulletin*, cccv., *of the U. S. Geological Survey*, then sifting, transferring the coarser matter again to the mortar, and repeating these operations till all had passed the sieve. Nevertheless, there was unavoidably much powder formed that passed 150 meshes and even 200 meshes to the inch. Material thus prepared and analysed was then ground in air, and also under water, absolute alcohol, or carbon tetrachloride, sometimes all three, in order to test the effect of these liquids, both on oxidation of iron aud absorption of water. The twenty-minute and thirty-minute grindings were all done by hand, those of longer duration by the McKenna mechanical grinder. Grinding by hand is less effective in producing fine powder than by a mechanical grinder for the same length of time, and different grinders may be very unequally effective (6, *c*, *d*). In comparing figures in the table it should be remembered that equal periods of grinding do not necessarily result in the production of powders of the same fineness, especially as between dry and wet grinding. Where more than one determination of water or iron was made on a given sample all are reported in order to show, more particularly, the generally excellent agreement of the iron values on a given sample when the rocks are readily decomposable and the variations to be expected when they are not. In the latter cases, finer grinding would have led to closer agreement but lower values.

All water percentages not otherwise indicated are based on direct weighings. If it were important to show the actual amount of water taken up by a given weight of unground material, the mode of statement would have been otherwise than by percentages of those weights. To give the percentages of ferrous oxide actually found would convey an incorrect impression. They have therefore been corrected by raising them in proportion to the amount of water absorbed during grinding, so as to be properly comparable with the percentages in the unground material, and give a true picture of the extent of oxidation suffered by the latter. These corrections range from 0 to 0·13 per cent. The same result would have been reached by reducing all FeO percentages to an anhydrous basis. In 1, 2, and 3 the FeO percentages in ground material are still too low, the full correction not being applicable for lack of data as to how much absorbed water was held at 110°.

Notes.

1. R. K. Meade, "Portland Cement," p. 307. In connection with the dehydration of gypsum, an interesting experiment made by Dr. E. C. Sullivan and Mr. Geo. Steiger in the laboratory of the U.S. Geological Survey, Washington, D.C., may well receive mention. They were able by grinding several hours daily for several days with a mechanical grinder to reduce the water of crystallisation of gypsum from 20 per cent to about 5 per cent, without evidence that a limit had been reached. It is regrettable that no effort was made to ascertain if this lost water could be regained by exposure to the air after grinding.

2. The following are the approximate diameters of the apertures in the sieves used :—

Mesh.	Mm.
80	= 0·20
100	= 0·18
120	= 0·11
150	= 0·08
200	= 0·065

These sieves were of metal, the use of which, in preparing samples for full analysis, is forbidden if traces of metals like those of which the sieve is made are to be looked for. In such cases, sieves of the best silk bolting-cloth shaken in a very gentle manner should be used.

(To be continued).

THE COMPARATIVE OXIDISING POWER OF SODIUM PEROXIDE AND ITS USE IN QUALITATIVE ANALYSIS.

By D. F. CALHANE.

The detection of chromium in qualitative analysis rests on its oxidation to the chromate and the precipitation of chromate of lead in acetic acid solution. The oxidation is usually effected by chlorate of potash on the solution of chromium hydroxide in strong nitric acid. If by any chance the nitric acid chosen is not strong enough or has become diluted, the oxidation will not occur, and the test fails. It is necessary for success that the hydroxides possibly containing iron, aluminium, and chromium be freed of water as much as it is possible by drying them quickly by heating. In this part of the procedure the student usually fails to work properly, not enough water is removed, and the subsequent oxidation does not occur. As I have found, in teaching classes in this subject, so much trouble in getting the student to properly observe precautions, it seemed of advantage to apply a test which would be effective and not so much dependent on a certain set of conditions.

Some experiments were accordingly made on the action

of certain other oxidising agents. Among these were chosen sodium peroxide and bromine water. The preference was for the former, as it is to be obtained in a convenient solid form, and possesses few of the disagreeable features of bromine water. A 0·1 N solution of chrome-alum was prepared, each cc. holding 0·0332 grm. of chrome-alum, answering to 0·005 grm. of Cr_2O_3. Next, the oxidation of portions of this solution with peroxide of sodium and bromine water was carried out to see what the comparative efficacy of these two reagents is on solutions containing known amounts of chromium. In this connection an interesting feature in the action of sodium peroxide on chromium solutions was met with, that at first led to the belief that bromine water was more efficient. The dilutions were carried to the point where the amount of chromic oxide present was only 0·000125 grm. corresponding to 0·000085 grm. of chromium. At this extreme dilution, a safe test was secured with bromine water, but the sodium peroxide apparently failed at a concentration answering to 0·00025 grm. chromic oxide. The bromine water appeared to act equally well both hot and cold at all the different concentrations from 0·005 grm. chromic oxide down to 0·000125 grm. With the sodium peroxide there was no test with the presence of 0·005 grm. chromic oxide, if the solutions were treated cold. When the sodium peroxide was added to the hot solution a small amount of yellow precipitate was obtained. An explanation of this surprising fact was arrived at later.

The next procedure was to find out what the limit of delicacy for the test is in actual analysis. Normal solutions of aluminium nitrate and ferric chloride were prepared, 1 cc. of which answered to 0·071 grm. aluminium nitrate and 0·054 grm. ferric chloride, giving a precipitate of 0·026 grm. aluminium hydroxide, 0·0356 grm. ferric hydroxide, and 0·0033 grm. chromic hydroxide from 1 cc. of the chrome-alum. The analysis in the first instance was carried through with a mixture of 1 cc. of each of the three solutions. The aluminium and iron here exceeded the chromium in the ratios of 8 and 12 times, respectively. The solution of the mixed salts was treated with 10 cc. of barium carbonate emulsion, and allowed to stand for two or three minutes. Next a filtration was made, and the filtrate tested for iron, chromium, and aluminium. The tests proved complete precipitation of the metals. The barium carbonate residue was dissolved in hot hydrochloric acid. The hydroxides of the three metals re-precipitated with ammonia. These were dissolved in hydrochloric acid, and the diluted solution divided into two equal parts. There could be present in each part the equivalent of 0·0025 grm. chromic oxide, answering to 0·0016 grm. chromium hydroxide. One part was added to a large excess of bromine water, after previously having added excess of sodium hydroxide. After filtration from the iron, no test for chromium appeared on adding acetic acid and lead acetate. In the other portion similarly treated, using sodium peroxide as the oxidising agent, a good test was obtained. Next, the above procedure was repeated, using 2 cc. of the iron and aluminium solutions and 1 cc. of the chromium. The ratios here were 24 iron, 16 aluminium, to 1 of chromium hydroxide. Here, again, the bromine water failed to act sufficiently for a test, while the sodium peroxide gave a good test. In the third experiment 5 cc. each of the iron and aluminium solutions were taken, and 0·5 cc. of the chrome-alum solution After proceeding as before, the bromine water failed to give a test, while 0·5 grm. sodium peroxide gave a reliable indication. The ratios here were 81 aluminium and 111 iron to 1 of chromium. The mixed precipitate contained 0·130 grm. aluminium hydroxide, 0·178 grm. ferric hydroxide, and 0·0016 grm. chromium hydroxide. In each of the last two tests the maximum amount of chromic oxide present for oxidation was 0·0008 grm., corresponding to 0·0005 grm. chromium.

In the next experiment it was desired to contrast the delicacy of the usual method with potassium chlorate and nitric acid with the peroxide procedure. Amounts taken were 5 cc. aluminium nitrate, 5 cc. ferric chloride, and 0·5 cc. chrome-alum. The analysis was carried through in the usual way, and the precipitate of iron, chromium, and aluminium hydroxides given by ammonia was dissolved in strong nitric acid, and boiled with potassium chlorate. The solution was divided into two equal portions, and one tested with sodium hydroxide acetic acid and acetate of lead. The result was negative for chromium. Here, as in the previous cases, 0·0008 grm. of chromium hydroxide was present. The result shows that the limit of successful oxidation by this method has been exceeded. The time required to carry this out is longer and the test is much less delicate than with the peroxide method.

Another test was made to compare the fusion method of oxidation with that using bromine water, potassium chlorate, and nitric acid and sodium peroxide. The usual method of fusing the hydroxides of iron, chromium, and aluminium mixed with dry potassium nitrate and sodium carbonate on platinum was followed, having present the same amount of chromium, iron, and aluminium as in the previous cases. The result here for chromium by the usual test as lead chromate after oxidation was surprisingly convincing. Five cc. of the ferric chloride aluminium nitrate and 0·5 cc. of the 0·1 N chrome-alum solution were precipitated by ammonia. The precipitate was filtered, washed, and fused in a platinum crucible with potassium nitrate and sodium carbonate mixture for a few minutes. The cooled mass was lixiviated with hot water. The iron was filtered off, and one-half of the clear filtrate, which was decidedly yellow, was made acid with acetic acid and lead acetate added. A good yellow colour was produced due to the formation of lead chromate. This test appears to be equally delicate with the sodium peroxide method. There was present in this fusion test 0·0008 grm. chromic oxide, or 0·0005 grm. chromium.

In the experiments having to do with the oxidation of the pure chrome-alum solution with bromine water and peroxide, it was surprising that the peroxide apparently failed to oxidise the chromium at a concentration where bromine water gave excellent results. It was, found, however, that if the solution was hot during the test a very slight precipitate of lead chromate was obtained with the sodium peroxide procedure. Bromine water acted equally well in hot or cold solution. It has been previously shown that in actual analysis sodium peroxide is by far the more powerful oxidising agent.

It was found on further experimentation that whereas a solution of bichromate was readily oxidised to perchromate by barium peroxide in acid solution, a chromic salt gave no indication of oxidation to the perchromate by the above agent. The chromic salt was only slightly oxidised to the chromate.

Sodium peroxide acting on a solution of the chromic salt gave a yellow colour. On acidification a violet colour appeared, which concentrated in ether indicated perchromic acid. In acid solution sodium peroxide gave no such oxidation. If a chromic salt were oxidised by sodium peroxide as above, the solution acidified with acetic acid, and lead acetate added, in dilute solutions such as were used in this work, no precipitate appeared. On allowing the solution to stand, or more quickly, on warming, the customary yellow precipitate of lead chromate appeared, and oxygen continued to be evolved for some time.

These results show the reason of the failure to obtain the tests for chromate of lead in the earlier part of the work where dilute solutions of chrome-alum were severally treated with sodium peroxide and bromine water. The sodium peroxide forms an alkaline solution with the evolution of oxygen. The chromic salt is oxidised to the perchromate, the sodium salt being formed in the alkaline solution. This substance is stable, and gives a yellow colour to the solution. On acidification with acetic acid, lead acetate produces no precipitate, as the lead perchromate is soluble in this medium. On standing or warming, oxygen is given off, and the lead perchromate breaks down to the chromate, giving the customary yellow precipitate.

Oxone, the fused form of sodium peroxide, acts the same

as the unfused variety, as would be expected. For analytical work it is less desirable, owing to the impurities it contains. In addition to the silica found in the unfused variety, it carries about 1·5 per cent of copper, as the result of several analyses showed. In addition small amounts of iron were found to be present. The results obtained in this investigation show that sodium peroxide is the best oxidising agent for chromium in solution. Sodium perchromate is formed by this agent in alkaline solution. This solution is stable, and, on acidification, oxygen is rapidly and continuously evolved. The oxygen can be liberated as fast as desired, thus giving a powerful oxidising source simply controlled.

The properties of this alkaline perchromate solution will be further investigated.—*Journal of the American Chemical Society*, xxx., No. 5.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

PART III.—ANALYSIS OF THE ALUMINIUM AND IRON GROUPS, INCLUDING BERYLLIUM, URANIUM, VANADIUM, TITANIUM, ZIRCONIUM, AND THALLIUM.

By ARTHUR A. NOYES, WILLIAM C. BRAY, and ELLWOOD B. SPEAR.

(Continued from p. 196).

Confirmatory Experiments and References (continued).

G. D., Section 6: Precipitation of Vanadium by Alkaline Hydroxides when Uranium is present.—For the insolubility of uranyl vanadate, see v. Klecki (*Zeit. Anorg. Chem.*, 1894, v., 381), Carnot (*Comptes Rendus*, 1887, civ., 1850); also C. E., *P. 58*a*, N. 3.

Fifty mgrms. V as Na_3VO_4 and about 250 mgrms. U as $UO_2(NO_3)_2$ were dissolved in 3 or 4 cc. HNO_3 (1·20) and 30 cc. water; the solution was made alkaline with NH_4OH (0·96); a large yellow precipitate separated. This was filtered off, and the solution was tested for vanadium by *P. 58*e*; not more than 1 mgrm. was found. In this experiment there was just sufficient uranium to form $UO_2NH_4VO_4$. The precipitate obtained in the preceding experiment was dissolved in a little HNO_3, diluted to about 15 cc., and poured into about 20 cc. 10 per cent NaOH solution; a large yellow precipitate separated. This was filtered off, and the filtrate tested for vanadium by *P. 58*e*; only 5 to 10 mgrms. V were found.

Separation of Zinc and Vanadium by Hydrogen Sulphide.—H_2S was passed into a solution containing H_3VO_4 and acetic acid; the solution slowly became blue, and sulphur separated, which rapidly became dark coloured owing to the precipitation of some V_2S_4.

One mgrm. V as Na_3VO_4 and 50 mgrms. Zn as $Zn(NO_3)_2$ were dissolved in 30 cc., a little acetic acid was added, and an excess of about 3 cc. NH_4OH (0·90). The clear solution was saturated with H_2S. A heavy precipitate of ZnS separated at once, and the solution slowly became deep red in colour, which colour was very distinct after filtering. The experiment was repeated with 1 mgrm. Zn and 50 mgrms. V; a precipitate of ZnS was obtained, which was confirmed by the last paragraph of P. 57.

Action of NH_4OH *on Uranium Solutions containing* H_2O_2.—100 mgrms. U as $UO_2(NO_3)_2$ were treated by P. 52. The red (peruranate) solution was made acid with HNO_3. Without heating, the acid solution (which contained H_2O_2, see C. E., P. 52, N. 6) was made alkaline with NH_4OH; a large yellow precipitate of $(NH_4)_2U_2O_7$ separated, but the filtrate was yellow. The filtrate was acidified with HNO_3, boiled for two or three minutes, and again made alkaline with NH_4OH; a large yellow precipitate separated, which was nearly as large as the first NH_4OH precipitate. The colourless filtrate was again acidified, boiled, and then made alkaline with NH_4OH; no precipitate separated. Therefore uranium, if present, will divide in P. 53.

To a nitric acid solution containing 200 mgrms. U as $UO_2(NO_3)_2$ and 40 mgrms. V as H_3VO_4 in 40 cc. were added about 20 cc. 3 per cent H_2O_2; the mixture was made alkaline with NH_4OH; no precipitate separated, showing that the precipitation of $UO_2NH_4VO_4$ and of $(NH_4)_2U_2O_7$ is prevented by the presence of an excess of H_2O_2.

Action of $BaCl_2$ *on Uranate Solutions.*—100 mgrms. U as $UO_2(NO_3)_2$ were treated by P. 52 and 53. The yellow filtrate from the NH_4OH precipitate, which contained about half the uranium, was treated by P. 55; a moderately large precipitate separated. After standing over-night the precipitate was filtered off, and the filtrate tested for uranium by adding HNO_3, boiling, and adding NH_4OH; a small yellow precipitate separated, which was estimated to contain 2 mgrms. U. Therefore barium uranate (or peruranate) may be precipitated nearly completely in P. 55.

Action of $BaCl_2$ *on Vanadate Solutions.*—100 mgrms. V as Na_3VO_4 were treated by P. 52 and 53. See C. E., P. 52, N. 10. The NH_4OH solution, which had a volume of about 40 cc., was made just acid with acetie acid, and $BaCl_2$ solution was added in the cold as described in P. 55; no precipitate separated from the yellow solution in five minutes. The experiment was repeated with 300 mgrms. V; no precipitate appeared when the $BaCl_2$ was first added, but in ten minutes a large orange precipitate of barium vanadate had separated. This was filtered off, and the filtrate allowed to stand over-night; a large precipitate formed. The precipitate was collected on a filter and washed with water; much of it dissolved, showing that barium vanadate is fairly soluble in water. A portion of the filtrate which was still slightly yellow was tested for vanadium by *P. 58*e*; much vanadium was found, showing that the precipitation of barium vanadates take place slowly, and that large amounts of vanadium remain in the filtrate in the cold. A solution containing 100 mgrms. V as Na_3VO_4 and a little NH_4OH in 40 cc. was made acid with acetic acid; 10 cc. 10 per cent $BaCl_2$ solution were added, and the mixture was boiled for a minute or two; a large nearly white precipitate separated, and the solution became perfectly colourless. The precipitate was filtered off, and the filtrate tested for vanadium by *P. 58*e*; the filtrate was found to contain not more than a few mgrms. of vanadium, thus showing that a large proportion of the vanadium had been precipitated on boiling. The last experiment was repeated, except that the acetic acid solution was made alkaline with NH_4OH, before boiling; the filtrate was found to be nearly free from vanadium. The last experiment was repeated, with a mixture of 100 mgrms. V and 10 mgrms. Zn as nitrate; only about 3 mgrms. Zn were found in the filtrate, showing that a large part of it had been precipitated with the vanadium, probably as zinc vanadate.

Action of NH_4OH *on Solutions containing Zinc and Vanadium as Vanadate.*—500 mgrms. Zn as nitrate and 100 mgrms. V as Na_3VO_4 were treated by P. 52; only a very small precipitate remained, and the solution was colourless. The filtrate was acidified with HNO_3 (1·20), an excess of about 2 cc. being added, and the solution was made just alkaline with NH_4OH; a large precipitate separated. Four cc. NH_4OH (0·96) were added; the precipitate dissolved completely. The NH_4OH solution was neutralised with acetic acid; a large precipitate separated, but it dissolved when a small excess of acetic acid was added. The acetic acid solution was boiled for a minute or two; a large precipitate separated, leaving a clear solution, which, however, still contained considerable zinc and vanadium.

Separation of Zinc and Uranium by NH_4OH.—One mgrm. Zn as $Zn(NO_3)_2$ and 100 mgrms. U as $UO_2(NO_3)_2$ were dissolved in 4 cc. HNO_3 (1·20) and 100 cc. water; the mixture was made alkaline with NH_4OH and an excess of about 3 cc. added; the yellow precipitate was filtered off, and the solution tested for zinc with H_2S; a small

* From the *Journal of the American Chemical Society*, xxx., No. 4.

nearly white precipitate separated. The experiment was repeated with 50 mgrms. Zn and 100 mgrms. U; the filtrate contained nearly all the zinc. The precipitate was washed, dissolved in HNO_3, diluted to 100 cc., and treated again with NH_4OH; the filtrate contained only about 2 mgrms. Zn. The NH_4OH precipitate was again treated in the same way; the filtrate contained no zinc.

Action of NH_4OH *on Solutions containing Uranium and Chromate.*—Four mgrms. Cr as K_2CrO_4 and 100 mgrms. U as $UO_2(NO_3)_2$ were treated as described in the preceding paragraph; the filtrate from the NH_4OH precipitate contained nearly all the chromium; the second NH_4OH filtrate was colourless. The experiment was repeated with 50 mgrms. Cr and 100 mgrms. U; the filtrate after the second NH_4OH precipitation was nearly colourless, thus showing that little or no chromium was carried down with the uranium.

G. D., Section 13*: Separation of Titanium and Zirconium by Boiling with Sulphurous Acid.*—With regard to the unsatisfactory nature of the process usually employed, see Hillebrand (*Bull. U. S. Geol. Sur.*, 1900, clxxvi., 72). A fairly satisfactory quantitative separation of titanium from iron is obtained by boiling a solution of a volume of about 1 litre containing acetic and sulphuric acids. This large volume is impracticable in qualitative analysis, and H. I. Wood and B. E. Schlesinger (Theses, Massachusetts Institute of Technology, 1901, 1902) devised the following method:—"Heat the HCl solution (volume 10 to 20 cc.) to boiling, remove the flame, add at once carefully NH_4OH until litmus-paper is turned distinctly blue, add 30 to 40 cc. H_2SO_3 solution, and place on the water-bath for fifteen to twenty minutes." This method was carefully tested by us. The results were satisfactory with titanium or zirconium alone, and small quantities of these elements were easily detected. But when iron was also present, some of it was carried down. In an experiment with 3 mgrms. Fe, 100 mgrms. Ti, and 100 mgrms. Zr as chlorides, no test for iron was obtained in the filtrate, thus showing that this amount of iron had been completely carried down. Also when 500 mgrms. alone (as $FeCl_3$) of Fe were present, some of the $Fe(OH)_3$ precipitated by NH_4OH did not dissolve in the H_2SO_3 solution, and even when ferrous iron was used, some $Fe(OH)_3$ sometimes precipitated during the heating on the water-bath. Moreover, the precipitation of titanium and zirconium was usually incomplete when much of these elements were present, more especially if the solution was not made distinctly alkaline with NH_4OH. This method is therefore a very unsatisfactory one.

G. D., Section 17*: Precipitation of Beryllium Phosphate as a Confirmatory Test.*—See B. E. Schlesinger (Thesis, Massachusetts Institute of Technology, 1902) Classen ("Ausgewählte Meth. d. Analyt. Chemie," 5th Ed., i., 715).

One mgrm. Be as $BeCl_2$ was in each of three experiments dissolved in water containing a little HCl; 1 cc. 10 per cent citric acid and 2 cc. 10 per cent ammonium phosphate solutions were added, the mixture was made strongly alkaline with ammonia, and it was boiled gently for about five minutes in a small flask; a small white crystalline precipitate separated. The experiment was twice repeated with 2 mgrms. Al as $AlCl_3$; no precipitate separated. The experiment was repeated with 0·5 mgrm. Be; no precipitate resulted (four experiments). Therefore this confirmatory test is hardly delicate enough, especially since beryllium has a very low atomic weight.

Test for Zirconium with Turmeric Paper.—The following procedure recommended by B. E. Schlesinger (Thesis, Massachusetts Institute of Technology, 1902) was tested:—"Dissolve the phosphate precipitate in HF (1 : 5), evaporate to one or two drops, and dip a piece of turmeric paper into it, heat the paper at 100° until dry." (Pink colour, presence of *zirconium*). In agreement with the results of Schlesinger, 1 mgrm. was found to be the limit of detectability. Even with 2 mgrms. the test was not a striking one. Moreover, titanium also caused a pink coloration of the turmeric paper, and the test was more delicate than in the case of zirconium. The blank test with strong HF was not perfectly satisfactory. The results obtained when HCl, instead of HF, was used were practically the same.

P. 51, N. 2: *Precipitation of Small amounts of various Elements by Ammonia.*—0·5 and 1 mgrm. of Al, Be, U, and Zr as nitrate, of Fe as $FeSO_4$, of Cr as $Cr_2(SO_4)_3$, of Ti as $TiCl_4$ were dissolved in separate experiments in 4 cc. HCl (1·12) and 30 cc. water in small conical flasks; the solutions were neutralised with NH_4OH (0·96), and about 1 cc. excess added; the mixtures were shaken several times, and then allowed to stand a few minutes; in each case the solution was transparent after the NH_4OH was added, but a distinct flocculent precipitate was observed after the shaking and standing. The precipitates were more difficult to see with chromium, aluminium, and uranium than with the other substances, but even in these cases 0·5 mgrm. was easily detected.

The experiments with aluminium, uranium, and chromium were repeated in a volume of 100 cc. containing 4 cc. HCl (1·12); 1 mgrm. Al was near the limit of detectability in a cold solution, but 0·5 mgrm. could be easily detected if the solution were heated nearly to boiling and allowed to stand. With uranium the limit of detectability was 1 to 2 mgrms. in a cold solution, and with chromium it was 2 mgrms. in a cold solution, but with 0·5 mgrm. Cr the solution became turbid on heating the NH_4OH solution to boiling.

Two mgrms. Cr as $KCr(SO_4)_2$ were dissolved in 4 cc. HCl (1·12) and a little water; the solution was boiled, diluted to 100 cc., cooled, and made alkaline with NH_4OH (0·96); a very small precipitate was seen after shaking and standing. This was filtered off, and the nearly colourless filtrate was heated to boiling; a finely divided light green precipitate then separated, showing that precipitation of $Cr(OH)_3$ by NH_4OH in the cold is incomplete.

Solubility of Zinc and Nickelous Hydroxides in Solutions containing NH_4Cl *and* NH_4OH.—To a number of solutions containing 500 mgrms. Zn as $ZnCl_2$, and varying amounts of HCl in 30 cc. of solution, known amounts of NH_4OH (0·96) were gradually added, 1·0 cc. HCl (1·12) being equivalent to about 1·5 cc. NH_4OH (0·96). The following table shows the amount of NH_4OH that had to be added (1) before a large precipitate was formed, (2) before a distinct odour of NH_4OH persisted after shaking, and (3) before the precipitate dissolved to give a colourless solution.

HCl (1·12) present.	NH_4OH (0·96) required.		
	To give a large precipitate.	To give a distinct odour.	To dissolve the precipitate.
Cc.	Cc.	Cc.	Cc.
2	3	8	11
4	7	11	14
6	11	14	16
8	No precipitate	17	—

The experiment was repeated in a volume of 100 cc. containing 4 cc. HCl (1·12); the result was practically the same as in the corresponding experiment with an initial volume of 30 cc.

The experiments were repeated with 500 mgrms. Ni as $NiCl_2$, the initial volume being 30 cc.; the solution became blue when an excess of NH_4OH was added, but no precipitate separated even when only 2 cc. HCl were used. In an experiment with no acid, a large green precipitate resulted, which dissolved on adding about 6 cc. excess NH_4OH after the odour of NH_4OH was persistent.

Precipitation of Cobalt Hydroxide.—The foregoing experiments were repeated with 500 mgrms. $CoCl_2$ and 4 cc. HCl (1·12) in 30 cc.; when the NH_4OH was added slowly a moderately large green precipitate was always obtained, which did not dissolve on adding a large excess of NH_4OH; the supernatant solution was reddish brown. The experiments were repeated with 4 and 6 cc. HCl (1·12), the ammonia (3 to 4 cc. excess) being added all at once; no precipitate was obtained, but the solution was red coloured, and darkened on standing owing to oxidation.

The experiments were repeated in a volume of 100 cc. containing 4 cc. HCl (1·12); the results were the same, except that the amount of green precipitate formed was greater than in the smaller volume, and that a larger excess of NH_4OH was necessary, in order to prevent the separation of a precipitate when the excess of NH_4OH was added all at once.

(To be continued).

CORRESPONDENCE.

PLATINUM IN SO-CALLED PURE BORAX.

To the Editor of the Chemical News.

Sir,—In the Chemical News for August 28th (vol. xcviii., p. 104) there is a reprint of a paper by Mr. J. G. Rose, Government Analyst, Cape Town, dealing with the discovery of traces of platinum in so-called pure borax. I should like to occupy a few lines in pointing out a serious inconsistency, not in the facts as set forth in the paper, but with an argument drawn from them. Mr. Rose has made a very careful assay of borax, and "alleges" that he has found platinum. Granted; from the evidence of thorough work which the paper shows we may consider the case fairly proved. But from this fact Mr. Rose goes on to infer that the recent discovery of platinum in this district may be wholly or partly due to impure reagents. He says, "In view, however, of the recent *allegations* (Italics are mine) regarding the occurrence of platinum metals in South African rock formations, the matter assumes a somewhat different complexion."

May I just detail these "allegations" of the presence of platinum in South African rocks. In 1906 two Grahamstown gentlemen, Dr. Purvis and Mr. T. H. Harrison, "alleged" that they had found platiniferous rock. In February, 1907, in an analysis of a sample of similar rock by myself, I "alleged" the presence of both platinum and gold; this, I believe, was the first analysis actually published. Since then Messrs. Johnson, Matthey, & Co. of London have assayed *some hundreds* of samples of rocks from this district, and have "alleged" the presence of platinum in over 70 per cent of them, from a few grains up to 19 ozs. per ton. The Standard Bank of Johannesburg made several assays, and in one instance "alleged" 80 ozs., and in another 286 ozs. per ton. In addition to these "allegations" there are many independent analyses from chemists and assayers in Grahamstown, Johannesburg, Glasgow, Swansea, London, and elsewhere, all confirming the presence of the platinum metals; further, on several occasions actual metallic platinum has been seen in the rock, and beads of platinum from 50 to 98 per cent pure obtained by chemical means; the largest amount so far extracted was an ingot weighing 4 dwts. When assayed in London it was "alleged" to be 98 per cent pure platinum. The only chemists of repute who have so far consistently failed to find the metal are the Cape Colony Government analysts, but I think that the evidence of the "alleged" existence of platinum far outweighs their negative testimony. As for the presence of platinum in borax, that will have no bearing when the platinum is extracted with aqua regia, chlorine, or similar solvents.

Considering that fifty or sixty companies have been actually formed locally with a capital representing half-a-million pounds or more; that active negotiations are being carried on for the flotation of one or two of these on the London market; that other companies are doing their best to discover a commercial process for the extraction of the metal, it looks as if, in the Colony itself, the "allegations" are considered fairly proved.

To put the matter in a nutshell, if Mr. Rose's unsupported testimony is sufficient to establish the fact that Merck's borax contains platinum, why are the hundreds of analyses made by numerous competent authorities only "allegations" of the existence of platinum in certain South African rocks?—I am, &c.,

E. G. Bryant, B.A., B.Sc.

Grey Institute,
Port Elizabeth, South Africa,
September 19, 1908.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvii., No. 10, September 7, 1908.

Fixation of Acetophenone by Benzoylacrylic Acid.—J. Bougault.—Boiling alkalis convert benzoylacrylic acid into glyoxalic acid and acetophenone, but if the acid is dissolved in a slight excess of alkali in the cold the reaction is different. On acidifying with acetic acid after twenty-four hours' contact a crystalline precipitate of diphenylacetic acid is obtained. The equation may be written—

$$2(C_6H_5—CO—CH=CH—CO_2H)+H_2O=$$
$$=CHO—CO_2H+(C_6H_5—CO—CH_2)_2=CH—CO_2H.$$

Probably the benzoylacrylic acid splits up into glyoxalic acid and acetophenone in the cold, but the change takes place more slowly than when heat is applied, and it is accompanied by the fixation of one molecule of acetophenone by one molecule of the undecomposed benzoylacrylic acid. Probably other acetones of the same type as acetophenone are capable of condensing with benzoylacrylic acid.

Nos. 11 and 12, September 14 and 21, 1908.

These two numbers contains no chemical matter.

MISCELLANEOUS.

Franco-British Exhibition, London, 1908.—It is officially notified that a Grand Prix has been awarded to the Wellcome Chemical Research Laboratories for their exhibit in Class 87 (Applied Chemistry and Pharmacy, &c.) at the Franco-British Exhibition.

Products from Milk-sugar and Calcium Hydroxide.—H. Kiliani.—The mixtures of milk-sugar and lime were freed from calcium salts of isosaccharine and metasaccharine, and from the mother-liquor all the calcium was removed by means of oxalic acid. The solution was then evaporated to a syrup, and extracted five times with absolute ether (Extract I.), four times with one part of absolute alcohol and two parts of dry ether (Extract II.), twice with a mixture of equal parts of the two solvents (Extract III.), and finally twice with absolute alcohol (Extract IV.). Each extraction was freed by distillation from the ether, and most of the alcohol then evaporated to a syrup and oxidised (II. and III. with concentrated nitric acid, IV. with the dilute acid). The first orientation experiments gave three oxidation products, *l*-tartaric acid, a tribasic acid $C_6H_8O_8$, perhaps identical with the acid of similar composition from isosaccharine, and a dibasic acid $C_6H_{10}O_7$, which differs from all known metameric acids.—*Berichte*, xli., No. 12.

NOTES AND QUERIES.

Ozokerite, Paraffin and Cerasin Waxes.—I should be obliged if any of your readers could tell me of any publication dealing with the chemical composition and analysis of ozokerite and paraffin and cerasin waxes.—A. Allender.

MEETINGS FOR THE WEEK.

Wednesday, 28th.—Society of Dyers and Colourists, 8. "Some Recent Improvements in Dyeing and Cleaning," by F. J. Farrell.

THE CHEMICAL NEWS.

Vol. XCVIII., No. 2553.

A RAPID METHOD OF QUALITATIVE ANALYSIS.

By W. B. POLLARD.

Walton and Scholz (*American Chem. Journ.*, xxxix., No. 7) have lately shown the value of sodium peroxide as a reagent for opening up ores and other refractory substances, their method being to deflagrate the substances with this reagent and a metallic sulphide. Noyes in his system of qualitative analysis has also used sodium peroxide for decomposing those substances which have escaped attack by acids (*Tech. Quart.*, xvi., No. 2), and for the separation of the metals of the ammonium sulphide group (*Journ. Am. Chem. Soc.*, xxx., No. 4).

The ease and rapidity with which substances are decomposed when deflagrated with sodium peroxide, together with the fact that when the resulting melt is dissolved in water and filtered, a sharp separation of the elements into two groups occurs, has suggested that this treatment might be made the basis of a system of qualitative analysis. The subdivision of each of the groups thus obtained might then be accomplished by means of the ordinary group reagents.

The decomposition of the substance by alkali instead of acid is therefore the essential characteristic of the method.

The advantages of this procedure may be stated as follows:—

1. The method can be applied to practically all substances.
2. Large quantities can be opened up with as much ease as small amounts.
3. All organic matter is destroyed.
4. The group separations are always done under standard conditions.
5. A great economy of time is effected.

It may be argued that a substance like hæmatite is not completely attacked when deflagrated with sodium peroxide. This would be fatal in quantitative work, but is not a serious drawback when we only require to know what elements are present in the substance; and, moreover, the process can be repeated on the undecomposed portion if desired. The fact that silicates, which constitute the chief portion of the earth's crust, are quite easy to examine in this way, but require special treatment when the ordinary system is followed, is a point strongly in favour of some such modification as the above.

It may also be said that if the substance is not first dissolved in some solvent, much useful information concerning its nature is lost. It seems more systematic, however, to find out first what elements are present and then to ascertain how they are combined, and to reserve this test till the end of the analysis.

As sodium peroxide attacks all materials it is necessary to arrange the reaction in such a way that metallic impurities are not introduced.

This can be done by making a mixture of approximately one part of the substauce, in the state of finest powder, with one part of vaseline and five parts of sodium peroxide, and igniting it on a thick iron plate, or in the cavity of a scorifying mould by means of a match or Bunsen burner. If the metal support is thick the heat is conducted away before the surface can become attacked. The excess of vaseline used also acts as a protection to the metal. The substance under examination should be dry, and the sodium peroxide used should be quite fresh, as samples which have been exposed to the air deflagrate very badly. Too much vaseline also should not be used, as the energy of the reaction is thereby considerably lessened. As a result of the action of the sodium peroxide, every element now exists in a definite condition in the melt, which is independent of the way in which it was formerly combined.

The melt is now dissolved in water and filtered, when a sharp separation of most of the elements into two groups is obtained. The soluble portion contains the soda salts of the metallic and non-metallic acids, for the most part in their higher states of oxidation, together with those oxides of the metals which are soluble in an alkaline solution. The insoluble portion contains the oxides, peroxides, and carbonates of the metals, any insoluble soda salts, and possibly a portion of the substance which may have escaped attack. A few elements like lead will be found in both portions, but this occasions no difficulty.

It must be noticed, however, that the results obtained by extracting the melt with water are not always the same as those obtained when a solution of the metal is precipitated with sodium peroxide. For example, on extracting the melt, titanium finds its way into the soluble portion, and small amounts of iron also dissolve under certain conditions.

Each of these portions can now be tested with the usual group reagents, but as the groups are smaller the recognition of the individual members becomes easier.

On dissolving the insoluble portion in acids, a little of the undecomposed substance may remain, together with the excess of vaseline, but these may be filtered out. A little phosphoric acid, which has not been rendered soluble by the action of the sodium peroxide, may also be present in the solution.

Instead of testing the soluble portion of the melt with the group reagents in the usual way, the following may often be sufficient:—The solution is first acidified with hydrochloric acid, when the colours due to the formation ot perchromic acid and titanium trioxide appear. The solution may then be neutralised with excess of soda, a little sodium sulphide added, and then boiled. On filtering out the metals precipitated by the sulphide, the solution may be again acidified with hydrochloric acid, and the sulphides of those metals, which form thio-salts, filtered out. A little silica may separate here, but this does not in any way interfere with the examination of the sulphides.

After oxidising the filtrate, aluminium may be precipitated by boiling with excess of sodium acetate and a little sodium phosphate. Potassium can then be precipitated in the filtrate as cobalti-nitrite. As, however, potassium is sometimes present as an impurity in sodium peroxide, this fact must not be overlooked when testing for that element.

Sodium must, of course, be looked for in the original substance, and mercury should also be tested for separately on account of its volatile nature.

In examining ores and minerals in the field, it is seldom necessary to test for more than two or three elements; the results, however, must be obtained quickly, and with the aid of a very limited supply of apparatus; in cases such as these the method may possibly prove of use.

A METHOD OF ANALYSING SHELLAC.*

By PARKER C. McILHINEY.

The method of analysis which is in most common use at the present time, both in England and in the United States, for the determination of the amount of rosin in shellac, is an indirect method depending upon the different powers of a shellac and of rosin to absorb iodine from a suitable solution. Different operators prefer different methods of making this test, some preferring to use the old Hubl method, and others the more modern Wijs method, as modified by Langmuir. Either of these methods is capable of giving reasonably satisfactory results, although the Langmuir method is certainly much to be preferred, both on the score

* Read before the New York Section, March 6, 1908. From the *Journal of the American Chemical Society*, xxx., No. 5.

of accuracy and of speed. Another method which is in use is that proposed by Parry, depending upon the solubility of the resinate of silver made from common rosin, in ether, while the corresponding resinates from shellac are insoluble. This method labours under several disadvantages and sources of error, of which the two principal ones are the solubility of the unsaponified portion of the shellac in ether, and the danger of a decomposition of the resinate of silver before it can be separated and determined.

A direct method of separating shellac and rosin and recovering the rosin, at least in a substantially unchanged form, is greatly to be desired, and several experimenters have attempted to make such a separation by taking advantage of the solubility of rosin in petroleum ether, a solvent in which shellac is insoluble. No method of extracting from even a finely pulverised sample of shellac the portion soluble in petroleum ether seems to be capable of removing more than a small part of the rosin contained in the sample.

Shellac dissolves in alcohol, except for the wax contained in it; petroleum ether dissolves to some extent in alcohol, and it was thought that by first dissolving the shellac to be analysed in alcohol, then adding to the solution all the petroleum ether which it would dissolve, and then adding water, so as to so dilute the alcohol that it would no longer have any material solvent power upon either rosin or shellac, there should result a separation of the dissolved petrolic ether containing in solution the rosin and the wax, but free from the resinous constituents of the shellac. Upon trying this process, it appeared that it was correct in principle, but that on account of the limited solubility of petroleum ether in alcohol, the separation was not quite complete. Upon substituting for ordinary alcohol, glacial acetic acid, or absolute alcohol, in which the sample of shellac to be examined is dissolved, and then adding to it petroleum ether, which is miscible in all proportions with acetic acid, or absolute alcohol, it was found practicable to combine with the rosin and the wax so large an amount of petroleum ether, that upon adding water, an almost complete separation of the rosin and wax from the resinous part of the shellac could be effected.

Based upon these facts, the following process was devised:—Dissolve in 20 cc. of glacial acetic acid (about 99 per cent), or the same volume of absolute alcohol, 2 grms. of the sample to be analysed. This requires a gentle heat. Add to the solution, after cooling, 100 to 300 cc. of petroleum ether, boiling under 80°. This addition of petroleum ether should be made slowly, because the addition of so large an amount of petroleum ether precipitates from its solution a part of the shellac, combined, apparently, in case acetic acid was the original solvent, with acetic acid to form a liquid precipitate. It is manifestly desirable that this precipitation of part of the shellac should not be effected by too sudden an addition of petroleum ether, as it might then contain some rosin carried down mechanically with it.

We now have a solution containing both petroleum ether and glacial acetic acid, or absolute alcohol, and containing in it, in solution, all the rosin, all the wax, and most of the resinous part of the shellac. Add now to this solution, drop by drop, 100 cc. of water, agitating the liquid during the addition. The water "unites with" the alcohol or acetic acid, and separates from the liquid the petroleum ether with whatever is soluble in petrolic ether. This includes the rosin and the wax. The shellac is also precipitated, but as it is insoluble in petroleum ether it remains as a precipitate suspended in the diluted alcohol or acetic acid. The separation of the two liquids takes place very rapidly, and it is an easy matter to effect a complete separation of the two layers in a separating funnel. The petroleum ether layer is washed once or twice with water, and then filtered through a dry paper into a weighed flask, from which the petroleum ether is then distilled off, leaving the residue of rosin mixed with wax, which is weighed. To the weighed residue neutral alcohol is added, and the flask heated to dissolve the rosin in the alcohol. The liquid is then titrated with N/5 or N/10 caustic potash. This gives a measure of the amount of rosin present, as the average combining equivalent of rosin does not vary greatly from 346. This is the figure used for this titration in the Twitchell process. It is much better, however, not to depend upon his determination of the rosin, but to proceed to an actual separation by adding to the neutralised alcoholic solution a distinct excess of alkali and a sufficient quantity of petroleum ether; the mixture is then transferred to a separating funnel, thoroughly agitated, and some water added. The liquids are then separated, the petroleum ether layer being washed with water, and the alcoholic solution of the rosin extracted once more with petroleum ether. The petroleum ether solutions are then united, the petroleum ether distilled off, and the residue of wax weighed. The alcoholic solution containing the rosin is then boiled until the alcohol has been expelled, and, if necessary, a further addition of water made; then dilute hydrochloric acid is added, so as to precipitate the rosin. This should be done in a weighed flask; the acidified liquid can now be decanted off through a wet filter-paper, so as to leave behind in the flask the major part of the rosin, which is washed with water. The remainder of the rosin upon the filter-paper after sufficient washing, is extracted with petroleum ether back into the weighed flask from which the water has been decanted as perfectly as possible. Upon distilling off the petroleum ether, the rosin is left behind in a condition to weigh. If the whole of the last traces of water have not been removed by the distillation with petroleum ether, it is well to add a further quantity of dry petroleum ether and distil again.

Attempts were made to use other solvents, particularly coal-tar benzene instead of petroleum ether. It was found, however, that benzene dissolved considerably more out of the shellac than the wax.

If it is desired to determine only the rosin in the shellac, it is unnecessary to distil off all the petroleum ether from the solution containing the wax and the rosin. This solution may, instead, be treated directly with an alkali capable of combining with the rosin, while leaving the wax unattacked. The most convenient method which I have found for accomplishing this is to add to the petroleum ether solution, after filtering it to remove from it anything which it may contain in suspension, a solution of sodium hydroxide in absolute alcohol. Such a solution I have found it convenient to make by dissolving in ordinary 95 per cent alcohol the appropriate amount of metallic sodium. Such a solution, when added to the petroleum ether solution, mixes perfectly with it, and the alkali combines with the rosin, and the mixed solution allows the saponified rosin to be extracted from it by agitation with water, or better, with slightly diluted alcohol. Instead of using a solution of sodium hydroxide in absolute alcohol, it should be possible to use the method of separating rosin from neutral substances in petroleum ether solution, that is used in the Twitchell process of determining rosin in admixture with fatty acid. This consists in agitating the petroleum ether solution with an alkaline aqueous solutions containing some alcohol, made by dissolving 1 grm. of potassium hydroxide with 10 cc. of alcohol in water, and diluting to 100 cc. I have found the other method of procedure advantageous, however, and believe it to give a more exact separation. The solution drawn off from the petroleum ether, after extraction by alkali, and containing in solution the rosin, combined with potassium or sodium, together with whatever alcohol has been used to promote the combination and to facilitate the mechanical separation of the two liquids, is heated for some time to remove the alcohol, and is then acidified with hydrochloric or with sulphuric acid to precipitate the rosin. The precipitated rosin is then weighed as before.

Without entering into a discussion of the exact chemical composition of shellac wax, it may be proper to state that the wax may be separated commercially from shellac by two essentially different methods, which will probably give waxes having somewhat different compositions. If the

shellac is dissolved in an alkaline solution and the wax which remains in suspension is filtered out, it is probable that different results will be obtained from what would be obtained by the other process, consisting of a solution of the shellac in alcohol, and filtration of the solution to remove the wax which will remain in suspension. It is to be expected that these two processes of solution would leave, in the undissolved wax, small amounts of ingredients of different characters, and, furthermore, the alcohol used in the second process would dissolve small amounts of the wax which would probably be quite insoluble in an alkaline aqueous solution. Again, it is quite probable that a caustic solution would behave towards shellac wax somewhat differently from a dilute carbonate solution. For the sake of uniformity and simplicity, I am assuming that shellac wax is quite free, when pure, from all acid substances capable of uniting with free alkali. It is nevertheless true that the user of shellac who wishes to have a determination made of the amount of wax which it contains, usually desires this information in order that he may know how much of the shellac will remain undissolved in alcohol. This amount of insoluble wax will, of course, vary to some extent, depending upon the strength of the varnish that he prepares with it; that is to say, the number of pounds of shellac which he uses to a gallon of alcohol. As the analyst can hardly be expected to take account of this in making his test, it appears more rational to regard as wax the whole of those matters contained in the shellac that remain insoluble in an alkaline solution.

In making a determination of the amount of wax in a sample of shellac by this method, it is to be observed that some constituent of shellac wax is evidently only difficultly soluble in petroleum ether. Upon submitting several portions of the same lot of shellac to analysis in this way, the only difference made in the different determinations being that varying amounts of petroleum ether were used, the series of analyses gave, with increasing amounts of petroleum ether, increasing percentages of wax, until the proportion of about 125 to 150 cc. of the solvent to 1 grm. of a shellac containing about 5 per cent of wax was reached. It may be that by using some other solvent such as benzene for the determination of wax in this way, a smaller amount will suffice, but as it seldom happens that only wax without rosin is to be determined, petroleum ether is the most generally applicable solvent. The solubility of rosin in petroleum ether is so easy and complete that no difficulty is experienced in extracting from 2 grms. of shellace 50 per cent of rosin, using 100 cc. of petroleum ether.

Whenever in the course of an analysis by this method a quantity of material is separated by acidifying the aqueous solution which should contain the rosin, its identity may be established with some certainty by determining its iodine figure by the Langmuir method, and its acidity by titrating with alkali in alcoholic solution.

The petroleum ether referred to here is a solvent made by re-distilling 71° Be benzine, separating for use that part which distils below 80°. This fraction constitutes a large proportion of 71° benzine, and such a re-distillation gives, at a comparatively small cost, a satisfactory solvent for the purpose. If a determination of only the rosin is desired, it is, of course, unnecessary to be very particular as to the volatility of the solvent used, as it is unnecessary in such case to distil it off before extracting the rosin by alkali.

By treating pure shellac according to this process, it is possible to separate from it a small amount, sometimes as much as 1 per cent, of materials soluble in petroleum ether. This small amount of resinous matter, when examined, proves to be something essentially different from common rosin. Its odour and its low iodine figure indicate that it is some resinous constituent of shellac, perhaps a small amount of the major constituent, which is slightly soluble in petroleum ether. As it is difficult to imagine that by this process rosin if a normal constituent of pure shellac would escape detection, and as the small amount of resinous matter here obtained is essentially different from rosin, it is reasonable to conclude that, contrary to the idea held by many, common rosin or a material similar to it, is not a natural constituent of pure shellac, but that any rosin or colophony, which can be separated in a state of reasonable purity from the sample of shellac, was originally added to the shellac as an adulterant.

The process here described allows the analyst to separate in a form convenient for exhibition either as evidence in court or as an ocular demonstration for his client, any rosin which may have been added as an adulterant to shellac.

Shellac varnishes may contain beside true shellac not only rosin, but other gums and resins soluble in alcohol. It becomes therefore a matter of interest to ascertain how some of these other resins behave when treated by this process. Two samples of manilla, when treated, using absolute alcohol as the first solvent, gave, respectively, 41·2 and 43·3 per cent of matter soluble in petroleum ether. The acidity of these two lots of matter soluble in petroleum ether was in the case of the first sample such that 1 cc. of normal alkali neutralised 411·7 mgrms., and in the case of the second 470·7 mgrms. Two samples of Kauri gave, respectively, 37·9 and 27·0 per cent. Upon titrating with standard alkali these portions soluble in petroleum ether, it appeared that 1 cc. of normal alkali was capable of neutralising 903·6 mgrms. and 742·5 mgrms. respectively. Of Sandarac, two samples, when similarly analysed, gave 34·96 and 36·19 per cent, having such an acidity that of the first, 541·2 mgrms. would neutralise 1 cc. normal alkali, and of the second 552·5 mgrms. would neutralise 1 cc. Of Dammar, 89·9 per cent proved to be soluble, while the resin of *Shorea roburta*, a sample of which was kindly sent by Mr. W. Risdon Criper, of Calcutta, gave 69·5 per cent of soluble matter.

A number of attempts were made to effect a satisfactory separation of the wax before separating the rosin from the shellac. It was found, however, that on account of the solubility of wax in alcohol and in glacial acetic acid, this separation could not well be made by filtering out the wax before the addition of petroleum ether. Neither were attempts which were made to separate the wax by a preliminary solution of the shellac in aqueous alkali successful in furnishing a method that at all approached in feasibility to the method already described.

THE WAVE THEORY OF MOTION.

By JOHN McDOWALL.

In the Chemical News, vol. xcviii., p. 61, I published a statement to the effect that motion could only be transmitted through the agency of a conducting medium.

The data on which this statement was based showed that the fundamental unit of matter was a wave of some kind, though it did not give any information as to the properties of the wave with respect to the velocity at which it was propagated through space. There were two possibilities, either the wave passed through space with a constant velocity which would be the normal wave, or else it ran at a speed proportional to its amplitude which would be abnormal.

I tried at first to get the normal kind of wave to fit in with the observed properties of the motion of matter, but failed to get a good explanation on those lines, and had to make use of a wave which ran at various speeds depending on its compression, as it seemed possible that the unique properties of the ether might make such a wave possible.

I have recently resumed work on the wave which runs at constant speed, and have overcome the difficulties which made me set it aside as impracticable before.

I shall put it before the reader in the same order as it was evolved so as to show why I abandoned it and how the difficulties were surmounted.

If we imagine two spheres to be passing through space

at a constant velocity in such a way that the paths which they make in space are parallel to each other, then they are relatively at rest with respect to each other; if we imagine the direction to be slightly changed, the sphere on the left being made to move towards the right, and the sphere on the right being made to move towards the left, then this would produce relative motion which would vary depending on the angle which the paths which the two spheres described in space made when produced to meet; the greater this angle the higher would be the relative velocity although the speed at which the spheres moved was constant.

Now it seemed that in this simple principle I had the key to the situation. Our ideas of motion are all of a relative nature, we know nothing of the absolute motion of matter in space. Any motion of the nature of a general drift of matter in space would be unknown to us because we would have no object absolutely at rest by which we could judge it; in fact, the motion common to all matter would be unknown to us, we can only recognise it when the motion is different in direction and velocity.

It would perhaps be best to introduce here the idea of the absolute resultant of the fundamental unit.

The absolute resultant of the fundamental unit is obtained by compounding any motion it has in the atom with the motion of the atom when agitated by heat, and the resultant of this with the motion of the earth round its axis, and the resultant of this with the motion of the earth round the sun, and the resultant of this with any drift which is common to the whole of matter, and on account of which we cannot recognise it, is most lucidly conceived as the imaginary line traced out by the fundamental unit in the ether as it passes through space and includes all and every motion that influences the fundamental unit. This is called the absolute resultant of the fundamental unit.

Let us return to the two spheres which can only move at constant speed, and instead of placing them so that the paths they describe are parallel to each other we place them behind each other so that there is a space between. Now, if the spheres were made out of matter whose fundamental units were waves which moved at constant speed, then when placed behind each other in this fashion they would not be able to vary the distance between them; if it was possible to give one an impetus it would only increase the amplitude of the fundamental wave, it would not make it move faster thongh it would take more force to stop it.

Now, instead of working with two spheres it will be convenient to work with a finite number, say ten or fifteen.

Suppose we consider a plane of two dimensions in which those spheres move, one dimension is devoted to the constant speed, the other to the relative speed.

Now, the only figure in which the spheres could move relatively and still remain in the region of collision would be represented by a line (in all those conditions it is necessary to consider the speed which is constant to be very much greater than the relative speed); if one sphere was placed out of line it could not collide with its neighbours.

Now, suppose we introduce another dimension, then the figure in which relative motion would be possible and the spheres be still within the region of collision would be represented by a plane. The spheres would be arranged on a plane which would move at right angles to its surface at constant speed, which must be very high compared to the relative motion of the spheres in the plane towards each other. Of course this relative motion will vary in velocity, depending on the inclination of the path of one sphere to that of a neighbour. This plane is important to remember.

Now, suppose we introduce another dimension yet, then the spheres would need to move with constant velocity in a certain direction, and over and above this there would be three dimensions in which varying inclinations of the path of the sphere to its neighbours would show up as varying relative velocity.

Now, we conclude from this that if this principle of constant speed and varying relative velocity is to be applied to explain the properties of motion in matter, then the whole bulk of matter must be speeding along a fourth dimension with constant velocity, which, if the rigidity of the ether goes for anything, must be very high—enormous, in fact—and that a minute deviation in the direction of the absolute resultant would show up as brisk relative motion, and a greater deviation as violent motion in the remaining three dimensions.

Now the question arises, if this dimension exists why do we not become aware of it? And this is what gave me much difficulty for a long time. If a man who was colour blind and could not see the red end of the spectrum was not told there was such a thing as red light, he would never be able to think that such a thing existed. We gain our knowledge of our surroundings by experience. Now, if we had a dimension in which we could not move, we would never be able to experience motion in it and would not be able to conceive it.

The difficulty is that there is a species of relative motion, which was the reason that I abandoned the theory at first, but on further investigation is one of the chief supports.

To go back to the standard plane on which the analogy is based.

We have the plane moving at constant speed in a direction at right angles to its surface. Now, if one of the spheres was to have an excess of relative motion its path would be more sinuous than the others, it would contain the same length for equal times but would contain less linear length of the dimension in which the plane moved with constant speed, and it would consequently drop out of line and be removed beyond the region of collision.

Now, the same thing should result with an additional dimension; that is to say, that a piece of matter which had a very high relative velocity should tend to drop behind matter with less, and should be removed beyond the region of collision. If the piece of matter had motion in its atoms, and fundamental units, then it would be removed gradually, for a unit whose motion reinforced the relative motion of the piece of matter would be left behind first, whereas a unit whose motion was opposite to the general motion of the piece of matter would take longer to be thrown behind. In fact, a body with excessively high relative velocity should leave a train of units behind it and gradually grow less in mass, and finally disappear in a mysterious fashion beyond the region of collision.

Now, there is no evidence to show that this happens; it is indeed a fact that it does not happen, for which reason, combined with the fact that the relative motion which would take place at high speeds was not observed, made me abandon this explanation and substitute the wave which moved with a velocity proportional to its compression, as that was the only kind of wave which would suit.

Now I have returned to the wave which runs at constant velocity with more success.

We have seen that relative motion must occur in this extra dimension to an extent depending on the relative velocity. This makes it possible for us to become aware of it. On the other hand, this extra dimension is an abnormal dimension. In the first place it contains the great bulk of the motion of matter. Our attitude towards it is, so to speak, "end on," whereas we are broadside on towards the other dimensions; relative motion in it can only be produced by producing an excess of relative motion in the ordinary dimension.

All those things show that this dimension is abnormal, so that it seemed possible that it would appear different to us than the other dimensions whose properties were all the same. It might, in fact, be well known to us, but we might look on it as something else. The next thing to do was to look for some principle which was of a fundamental nature, and which might be the extra dimension in disguise.

It should be closely associated with ordinary space and

also motion, and might possibly show the disturbe reflection of a dimension in it.

Now the only principle which seems to meet those conconditions is time. Time must clearly have an objective reality; the fact that we can measure it shows this. Time has one dimension. We speak of a length of time, and a space of time, and although our conception of this is different from our conception of a length of space the abnormal properties of matter might explain this.

In order to test this we have to see exactly the relations of time to motion and to ordinary space, and then see if those same relations hold for the extra dimension.

Suppose we measure off a finite length of an ordinary dimension, say, thirty metres; now suppose we send two projectiles over this space, one projectile being a bullet from a gun, the other being thrown by hand.

Both those projectiles would do the same act with respect to the space—they would both move over it, but while doing this they would differ on two points. The bullet would contain a much larger quantity of relative motion than the other projectile, and would also consume a smaller length of time.

Now, how would the fourth dimensions act under those same conditions? The result of superposing on the absolute resultant different quantities of relative motion is to make it more oblique; with respect to the fourth dimension it moves slower along it and consumes less of it than if a smaller quantity of relative motion had been used. This shows there is a connection, but does not establish the identity of the two.

This may be done as follows:—Suppose two men had to meet at a certain place, what are the mechanical conditions which such a meeting involves? From an absolute point of view the two men would meet when their absolute resultants intersected, both men being at the point of intersection.

Suppose we do not take the fourth dimension into account, simply fixing a point in the ordinary dimensions, then both men would do the act of passing over the space to this point; perhaps one would pass an hour after the other, and they would not meet. This shows that to fix their absolute resultants rigidly another condition is needed; by simply fixing the point of meeting in the ordinary dimensions there is a degree of freedom, and this degree of freedom is along the fourth dimension. It is therefore obvious that if we have to make their meeting a mechanical certainty that we have to fix them in respect to this dimension. Also when this is done their absolute resultants as far as they concern each other are rigidly fixed, and meeting is a mechanical certainty.

We have, in fact, to make them on a level in the fourth dimension, and also make them pass over the ordinary dimension to the point of meeting. When those conditions are attended to then they will meet, the absolute resultant being rigidly fixed in space.

Now if they are not on the same level in the fourth dimension, how are they to manage to get level?

Let us go back to the standard plane on which the analogy is based. We have the plane moving at constant speed. Let us imagine one sphere to be placed in front of it moving at the same speed, and another to be placed behind, how are those two spheres to get into the plane?

The one in front can do so by pursuing a sinuous or oblique path, which means that it lets out a large quantity of relative motion, and enables the plane to draw up on it; the sphere behind would do the opposite, describing a path containing less relative motion than the average relative motion of the spheres in the plane, and would catch up on it. Now, the men in order to get on a level in the fourth dimension must do the same thing while proceeding to the appointed place; if they are not on a level one of them must let loose a large amount of relative motion and the other a small amount, both doing the required act with respect to the ordinary dimensions by moving across the space to the point of meeting. Now the means by which they know if they are on a level is by means of a watch, and the one who is late produces a large amount of relative motion, and the one who is early a amall amount, doing this to the proper extent, and they meet.

Two bodies are removed as securely from the region of collision if they cross the same point at different times as if they were in a different part of space.

Our minds are constructed to think and conceive this fourth dimension as time, and the other three as space, because the properties of the motion of matter to this dimension is different to the others, and therefore we conceive it in a different way so as to accommodate ourselves to the different properties of motion towards it.

There is another thing I should like to note before concluding this short statement, and that is the property of projectiles or other bodies to be as a system in a state of relative rest to an object a long distance away if they described enclosed curves.

If we had the two men at a distance from each other in a state of relative rest, then if one of them described small ellipses, no matter how much relative motion he let loose he would still be in a state of relative rest; as a system when the axes of the ellipse was very short compared with the distance of the other man if he had let loose the same amount of motion in a straight line, he would be in a different position to the other man, not only with respect to the ordinary dimensions but also to the fourth dimension—time.

Now the reason that he is in a state of relative rest while describing an enclosed figure is because he undoes in one part of the curve what he does in the other.

This absolute resultant, if he was in a state of relative rest, is in a certain direction; as he begins to move in an ellipse when he moves away from the observer he superposes on this resultant a component which makes it more oblique along the fourth dimension; on the return he superposes a component which makes the absolute resultant abnormally straight along the fourth dimension; so we have simply positive and negative accelerations in the fourth dimension which balance each other, and the body as a whole is at relative rest, so we can bottle up relative motion by making the units of matter describe enclosed curves, and, of course, the same thing holds for the planes and other bodies which as systems are at relative rest.

Sebaieh, Upper Egypt.

THE INFLUENCE OF FINE GRINDING ON THE WATER AND FERROUS-IRON CONTENT OF MINERALS AND ROCKS.*

By W. F. HILLEBRAND.

(Concluded from p. 206).

Effect of Grinding in Air.

The table shows in the first place with respect to the moisture, that while some rocks and minerals contain in the lump, and even in material as fine as 100-, or even 120- and sometimes 150-, mesh size, little moisture (2*a*, 5*a*, 12*a*, 13*a*) or none at all (14*a*, 15*a*), many, and particularly those that have undergone more or less alteration into hydrous minerals, contain in coarse condition a good deal of loosely held water (3*a*, 4*a*, 6*a*, 8*a*, 9*a*). Since this water is characteristic of certain minerals and affords a valuable index of the character and extent of alteration or of the presence of zeolitic minerals, it should not be excluded from the tabulated analysis, as Mauzelius recommends. On the other hand, the petrologist reports "kaolin" as the chief hydrous mineral in 13. The analysis shows absence of loosely held water, therefore the mineral is probably in the crystallised form of kaolinite, which does not lose water at 100°. Since, further, such powders of grain as coarse as 100-, 120-, and even 150-mesh often show much

* From the *Journal of the American Chemical Society*, xxx., No. 7.

No.	Material.	Maximum grain of bulk sample.	Exp. No.	Conditions of grinding. Grms. of bulk sample.	Enveloping medium.	Time, minutes.	H_2O per cent. 105°−.	H_2O per cent. 105°+.	FeO per cent, corrected for H_2O taken up. Pratt method.		Cooke method.	
1.	Basalt*	0·08 mm. < 150-mesh	*a*	Unground	—	—	0·24	—	7·03	7·07	—	—
			b	4	Absolute alcohol	30	0·34	—	7·09	7·11	—	—
									7·09	7·12	—	—
			c	4	Air	30	0·32	—	7·14	—	—	—
									7·01	7·07	—	—
									7·08	7·16	—	—
									7·18	7·23	—	—
			d†	20 ?	Air	?	0·45	—	7·12	—	—	—
			e	4	Air	120	0·83	—	6·87	6·93	—	—
2.	Diorite‡	0·08 mm. < 150-mesh	*a*	Unground	—	—	0·07	—	3·65	3·65	3·55	3·52
			b	4	Absolute alcohol	120	0·32	—	3·48	3·50	3·41	3·50
			c	4	CCl_4	120	0·48	—	3·30	3·37	3·26	3·31
			d	4	H_2O	140	0·53	—	3·41	3·44	3·37	3·39
			e	4	Air	120	0·54	—	3·29	3·37	3·30	3·39
									3·41	—	—	—
			f†	20 ?	Air	?	0·28	—	3·52	—	3·37	—
3.	Andesite	0·08 mm. < 150-mesh	*a*	Unground	—	—	1·14	—	2·57	2·58	—	—
			b	4	Absolute alcohol	15	1·21	—	2·58	—	—	—
			c	4	H_2O	15	1·39	—	2·53	—	—	—
			d	4	Air	15	1·46	—	2·53	—	—	—
4.	Andesite	0·08 mm. < 150-mesh	*a*	Unground	—	—	1·01	3·40	3·32	3·34	—	—
			b	4	Air	30	1·18	3·54	3·09	—	—	—
5.	Diabasic norite or gabbro§	0·08 mm. < 150-mesh	*a*	Unground	—	—	0·03	0·66	13·55	13·35	13·54	13·24+
			b	4	Absolute alcohol	20	0·10	0·86	13·04	13·14	13·11	—
									13·15	13·20	—	—
									13·23	—	—	—
			c	4	CCl_4	60	0·34	0·94	12·95	13·00	—	—
			d	4	Air	30	0·10	0·66	12·91	12·93	13·06	13·07
									13·06	13·07	—	—
			e†	20 ?	Air	?	0·10	0·65	—	—	—	—
			f‖	4	Air dried by H_2SO_4	120	0·74	1·00	12·72	12·79	—	—
6.	Diorite-porphyry . .	0·18 mm. < 100-mesh	*a*	Unground	—	—	0·29	1·97	2·71	2·72	—	—
			b	20 ?	Air	?	0·42	2·07	—	—	2·38	—
			c	4	Air, machine A	120	0·91	2·26	2·30	2·31	—	—
			d	4	Air, machine B	120	1·90	2·73	1·54	1·54	—	—
			e‖	4	Air-dried by H_2SO_4, machine B	120	1·36	2·38	1·80	—	—	—
7.	Altered basaltic greenstone	0·18 mm. < 100-mesh	*a*	Unground	—	—	0·22	3·13	6·68	—	—	—
			b	4	Air	120 or more	1·70	4·19	3·74	—	—	—
8.	Quartz-diorite	0·11 mm. < 120-mesh	*a*	Unground	—	—	0·37	2·03	2·58	—	—	—
			b	4	Air	120 or more	1·08	2·33	1·69	—	—	—

9.	Quartz-diorite	0·11 mm. < 120-mesh	*a*	Unground	—	—	0·35	1·60 1·64	2·08	2·09	—	—
			b	4	Absolute alcohol	120	0·54	1·80	2·02	2·02	—	—
			c	4	Air	30	0·40	1·56 1·64	2·04	2·07	—	—
			d	4	Air	120	1·01	1·86 1·95	1·48	1·48	—	—
10.	Quartz-diorite	0·11 mm. < 120-mesh	*a*	Unground	—	—	0·21 0·22	0·65 0·65	2·55	2·58	—	—
			b	4	Absolute alcohol	120	0·39	0·88	2·58	2·58	—	—
			c	4	CCl_4	120	0·41	0·80	2·47	2·51	—	—
			d	4	Air	120	0·69 0·70	1·05	2·33	2·34	—	—
11.	Granite	0·11 mm. < 120-mesh	*a*	Unground	—	—	0·12	0·46	2·28	2·28	—	—
			b	20?	Air	120 or more	0·21	0·53	1·85	—	—	—
12.	Granite	0·11 mm. < 120-mesh	*a*	Unground	—	—	0·03	0·24	1·93 2·08	2·01 —	—	—
			b	4	Absolute alcohol	120	0·32	0·64	2·01 2·06	2·03 —	—	—
			c	4	Air	120 or more	0·67	0·72	1·86	1·86	—	—
13.	Altered basaltic rock..	0·18 mm. < 100-mesh	*a*	Unground	—	—	0·03	2·00 2·12 2·15	8·33	8·34	—	—
			b	4	Absolute alcohol	120	0·54	2·42	8·18	8·21	—	—
			c	4	Air	30	0·15	2·19	8·24	—	—	—
			d	20?	Air	Not known, but very long.	1·16 1·21	3·34 3·36	5·86	—	—	—
14.	Quartz	Mostly finer than 0·08 mm. < 150-mesh	*a*	Unground	—	—	None	0·06¶	—	—	—	—
			b	4	Air	120	0·35	0·45	—	—	—	—
15.	Berlin porcelain, unglazed**	?	*a*	Uncrushed	—	—	None	None	—	—	—	—
			b	?	Air	?	0·62	0·18	—	—	—	—
16.	Meerschaum††	Coarse	*a*	Unground	—	—	5·76	6·79	—	—	—	—
			b	4	Air	600	6·33	9·81	—	—	—	—

* The rather wide variations for FeO in the same series, particularly *c*, are ascribed to the refractoriness of an iron-bearing constituent, which necessitated several re-treatments.

† Sample originally analysed.

‡ Difficult to decompose by HF in powder coarser than 150-mesh.

§ An iron-bearing garnet in this rock was extremely refractory unless very finely ground.

‖ Exposed to air of room after grinding.

¶ H_2O 105°+, by ignition.

** Also 0·80 per cent H_3O as total ignition loss.

†† Tests made in 1902.

less than 0·1 per cent moisture, if hydrous alteration products are absent, it is reasonable to conclude that there has been occasioned relatively as little oxidation of iron in such powders as absorption of moisture, on the assumption that the small amount of water found results from the increased surface exposure due to crushing, and is not inherent. Therefore, if the powder is completely decomposed by hydrofluoric acid, it is safe to assume that a determination of ferrous oxide in it, carried out with proper precautions, will give a result close to the truth.

It is further evident that, whereas long grinding in air (two hours or more) by the mechanical grinder in most cases gives rise to marked oxidation of iron (6*d*, 7, 8, 9*d*, 11, 13*d*), and increase in the water content (6*d*, 7, 8, 9*d*, 10*d*, 13*d*, 14) these effects are usually not strongly marked when the grinding was by hand for only thirty minutes or less (5*d*, 9*c*, 13*c*, and especially 1*c*, *d*) though almost invariably plainly enough revealed by the tests to forbid grinding when the highest accuracy is of importance. Occasionally, as in 3*d*, fifteen minutes' grinding resulted in relatively appreciable oxidation of iron and absorption of moisture.

It is further very evident, as noticed by Mauzelius, that with different minerals very different degrees of oxidation result under like conditions, from a few per cent (1*e*) up to nearly 50 per cent (7) of the FeO after several hours' grinding, and it is not always the mineral that might *à priori* be regarded as most oxidisable that shows most oxidation. For instance, a magnesian siderite containing 46 per cent FeO, tested by myself, suffered oxidation of only about 3 per cent of its FeO when ground by itself for fifteen minutes, and but little over 5 per cent when ground for two hours with four times its weight of quartz powder. The nearly white colour of the original powder had, however, become decidedly brownish in both cases. It is undoubtedly true that, as shown by Mauzelius for mica, a soft or tough mineral undergoes greater oxidation if ground together with a hard one, like quartz as in the above instance, and with the mica tested by him, than by itself. This is due, of course, to the attrition effect of the harder mineral; hence, in different rocks the extent of oxidation of one and the same ferrous mineral may depend on the nature of its associates. Naturally the degree of water absorption will be less or greater for a like reason. Relatively slight oxidation of FeO after grinding in air (1, *c*, *d*) may sometimes be due to the hardness of the iron-bearing minerals or their toughness in absence of other hard ones, which would result in a far coarser powder than with some other rock or mineral ground for the same length of time, but in addition the relative stability of the chemical molecule is doubtless an important factor, perhaps the most important. Much remains to be done in accumulating experience with different minerals and their mixtures.

Naturally the idea of grinding in an inert atmosphere suggested itself, in order to prevent if possible the oxidation of FeO, if not the absorption of water. If the oxidation is due to local heating more than to surface exposure, this treatment should be effective in reducing or preventing it, and it is hoped to put it to the test for the purpose of settling the point more than with any hope of providing a practical means of preparing fine powders that shall be chemically unaltered. One test has already been made of grinding the siderite already mentioned in an atmosphere of carbon dioxide, which is suggestive, though not conclusive, because it was found impossible under the conditions to secure complete exclusion of air from the box in which the grinding was done. After two hours' grinding and subsequent thorough exposure to the air, the powder was darker than the unground material or than that ground under alcohol, but decidedly lighter in colour than that which had been ground for only hour in full contact with air. The inference is that local heating plays an important part in promoting oxidation. That an inert atmosphere would not be effective in preventing absorption of water was apparent, and was clearly shown by experiments 5*f* and 6, *d*, *e*, in which the grinding was done mechanically in an atmosphere dried by sulphuric acid, the mortar with its coarse powder having been placed in its housing together with vessels of sulphuric acid several hours before the grinding commenced, and a current of dry air passing through during the whole of the operation. The powder (6*e*) was then, after exposure to the air of the room for several hours, found to contain nearly as much water, loosely and firmly held, as when ground by the same machine for the same length of time in undried air. That the amounts were not fully as great is of little importance in view of the varying effectiveness of the different grinders, and even of the same grinder on different days.

Effect of Grinding under Liquids.

The results of grinding under different liquids are of interest, though not conclusive by reason of the limited number of tests that have been made. The results referred to in the foregoing paragraph rendered it unlikely that with the same degree of comminution there would be any material decrease in the amount of absorbed water, and experiments served only to confirm this view. They did show, however, that the effect was to materially reduce the oxidation of the iron, water being in this respect apparently somewhat less effective than absolute alcohol or carbon tetrachloride. A striking effect of the carbon tetrachloride may be mentioned. The mineral powder in contact with it becomes highly flocculated, and settles out at once when the grinding is interrupted, leaving a perfectly clear liquid above, in marked contrast to the lack of such effect with water and alcohol. As between the two named organic liquids, alcohol seems to be the more effective in preventing oxidation (2*b*, *c*, 5*b*, *c*, 10*b*, *c*) if we assume that the same degree of subdivision was reached with both in like periods of time, therefore the tests with carbon tetrachloride were not multiplied.

When alcohol was used, in most cases (1*b*, 3*b*, 10*b*, 12*b*) oxidation seems not to have taken place, even after two hours of continuous operation of the machine in the last two instances, at least not to a determinable extent. This again seems to be rather strong evidence that it is not increased surface exposure merely that gives rise to the marked oxidation of FeO when ground in air, but that local heating of the grains in contact with oxygen as they undergo crushing is the important factor. Were it not so, it would seem as if the iron should undergo oxidation after removal of the alcohol and exposure to the air, just as it then takes up water, but this it does not seem to do. In 2*b*, 5*b*, 9*b* for no evident reason the alcohol seems to have been less effective, taking always the FeO content of the crushed but unground bulk sample as the standard to go by. On the whole, this method of securing a fine sample does not altogether commend itself, since, while eminently satisfactory sometimes, the error affecting it is appreciable at other times. Nevertheless, it may give good service on occasion; hence the procedure to be followed in using it will be given. The coarse powder is covered in the mortar with absolute alcohol that leaves no residue whatsoever on evaporation. The amount used should not be more than enough to form a very liquid emulsion during the operation of grinding. One or two additions of alcohol may be needed if the grinding has to be of long duration. The grinding should be continued in any case till the mass becomes somewhat thick, then the mortar and pestle are left to dry by unaided evaporation of the excess of alcohol, a wide glass being supported above the mortar to keep out dust without too much impeding air circulation. When supposed to be thoroughly dry, the powder is transferred in its entirety to a watch-glass, and placed on the balance-pan, where it is to be kept till it is quite evident that no further loss in weight takes place. It is then transferred to a sample tube.

Application of the foregoing Results to Mineral Analysis.

It is plain from what has been said that nearly all mineral analyses that have been made in the past are affected by

more or less serious errors in respect to water and the oxides of iron, the error being greater the farther the comminution of the sample was carried. Very many analyses show more ferric iron in minerals that should apparently contain none, and small amounts of water for which there seems to be no place in any probable formula. These are discordances for which a simple and in most cases probable explanation now offers. A revision of much past analytical work, particularly that relating to iron-bearing minerals, is called for, but before it can be properly done, adequate provision must be made to avoid the old errors. In the paragraphs following will be set forth the procedures that seem best adapted to secure this end, in the light of present experience. It is perhaps advisable to add here, in order to avoid misconception, that the errors in past work are not, as a rule, to be assumed equal to those in the table that resulted from grinding for two hours or more, for few, if any, analysts have made it a rule to grind for such a length of time.

Treatment of Sample in First Stage of Analysis.—The mineral powder, prepared by careful crushing without grinding (see *ante*) serves as the starting-point. If it is possible to effect complete or nearly complete decomposition within thirty minutes by dilute hydrofluoric acid with powder so coarse as just to pass a sieve of 80 meshes to the linear inch (about 0·20 mm. diameter of apertures), a powder of this degree of fineness should be used in preference to one finer. In general, such a powder can be used without grinding for all determinations that involve fusion with an alkali carbonate, but not always. If finer grinding, either in air or under alcohol (see above) is imperative, it will be necessary with the ferrous iron portion, when there is enough of this constituent to make an appreciable difference, to make water determinations on the finely-ground as well as on the coarse powder, in order to be able to reduce the results obtained for the ferrous oxide to the weight represented by the coarse powder. For other constituents, as the alkalis, this course will not generally have to be followed; it will be sufficient to take of the coarse sample a weight called for by the particular determination, and to grind this in a large mortar with extreme care to avoid loss by dusting or flying of grains, and then to cleanse the mortar by grinding in it a little of the flux that is to be subsequently employed, or of some harmless material other than a flux, the rinsings being added, of course, to the main portion of the fine powder.

For the ferrous iron determination two courses are open: —(*a*) To grind under alcohol until a degree of fineness is reached that will surely admit of complete decomposition by boiling dilute hydrofluoric acid within fifteen or twenty minutes; (*b*) to treat the coarse powder directly with hydrofluoric acid. If a single treatment by (*b*) does not effect complete decomposition, and this will be very often the case, the procedure that has thus far commended itself is the following:—Having titrated (according to the directions in *Bull. U.S. Geol. Survey*, cccv., 142) with permanganate to the first more or less transient pink blush throughout the whole body of liquid, let settle, decant, and wash once by decantation with water, rinse the residue into a small agate mortar, decant most of the water after again allowing to settle, grind the residue for a short time under what water remains, transfer it by a stream of hot water to the large crucible from which it was taken, and repeat the treatment by hydrofluoric and sulphuric acids used in smaller amounts than the first time. The final titration may be made in the crucible itself if this is of at least 80 cc. capacity and the bulk of liquid in it is small, after quickly diluting with cold water till the crucible is nearly full.

This manner of treatment has afforded thus far satisfactory results, and is in most cases to be preferred to that given as (*a*). Not only are the double determinations of water avoided, but also the error that often arises from oxidation by long grinding under alcohol. The very short grinding under water of the small fraction of the original iron-bearing mineral or mineral that remains after the first treatment with hydrofluoric acid cannot conceivably lead to any detectable error.

In conclusion, a few remarks are in place regarding the comparative merits of the Pratt and Cooke methods of decomposing minerals for the ferrous iron determination. In *Bull.*, cccv., 138, it was said that indications seemed to slightly favour the former method, and this expression is strengthened by the comparative data contained in the table. Although in some instances (2, *b*, *e*, 5, *a*, *b*, *d*) the two methods appear to be of equal merit, in others (2, *a*, *f*) they differ materially in favour of that of Pratt, and in the rest there is evident a general tendency toward lower results by that of Cooke.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

Part III.—Analysis of the Aluminium and Iron Groups, including Beryllium, Uranium, Vanadium, Titanium, Zirconium, and Thallium.

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(Continued from p. 210).

Confirmatory Experiments and References (continued).

Solubility of Aluminium Hydroxide in Excess of Ammonia.—To a solution containing 10 mgrms. Al as nitrate and 4 cc. HCl (1·12) in 100 cc. were added in the cold 17 cc. NH_4OH (0·96); *i.e.*, an excess of about 10 cc., and the mixture was shaken; the precipitate of $Al(OH)_3$ was filtered off after about five minutes, and the filtrate was boiled for several minutes to expel the excess of NH_4OH; a precipitate of $Al(OH)_3$ separated which was estimated to contain about 3 mgrms. Al. The experiment was repeated, except that an excess of only 2 or 3 cc. NH_4OH (0·96) was used; the filtrate on boiling became turbid, but the amount of aluminium that separated did not exceed 0·5 mgrm.

P. 51, N. 3 *and* 4: *Solubility of* $Mg(OH)_2$ *in* NH_4Cl *Solutions.*—The solubility of $Mg(OH)_2$ in water is about 2×10^{-3} mols. per litre. For evidence that the non-precipitation of $Mg(OH)_2$ in moderately dilute solutions containing an ammonium salt depends solely on the driving back of the dissociation of NH_4OH, see Lovén (*Zeit. Anorg. Chem.*, 1896, xi., 404), Treadwell (*Zeit. Anorg. Chem.*, 1904, xxxvii., 326), Herz and Muhs (*Zeit. Anorg. Chem.*, 1904, xxxviii., 138).

The following experiments show that enough ammonium salt is produced by the neutralisation of the 4 cc. HCl (1·12) originally present to prevent the precipitation of $Mg(OH)_2$ even when 500 mgrms. are present. A solution containing 500 mgrms. as $MgCl_2$ and 4 cc. HCl (1·12) in 100 cc. was neutralised with NH_4OH (0·96, 6 cc.), and more NH_4OH was added. No precipitate formed when 40 cc. in all had been added, but the addition of 10 cc. more gave a precipitate. The experiment was repeated with an initial volume of 30 cc. instead of 100 cc.; 30 cc. NH_4OH produced no precipitate, even after several minutes, but 40 cc. did. The experiment was repeated with 2 cc. HCl and a volume of 30 cc.; 15 cc. NH_4OH (0·96) produced no precipitate, but 20 cc. did.

Complex Zinc Ammonia Cation.—$Zn(NH_3)_4{}^{++}$. See Herz (*Zeit. Anorg. Chem.*, 1900, xxv., 225), Gaus (*Zeit. Anorg. Chem.*, 1900, xxv., 236), Euler (*Ber.*, 1903, xxxvi., 3400), Bonsdorff (*Zeit. Anorg. Chem.*, 1904, xli., 132).

Complex Nickel Ammonia Cation.—$Ni(NH_3)_4{}^{++}$.—See Dawson and McCrae (*Journ. Chem. Soc.*, 1900, lxxvii., 1239), Konowaloff (*Chem. Centralblatt*, 1900, i., 646), and especially Bonsdorff (*Zeit. Anorg. Chem.*, 1904, xli., 132).

Behaviour of Chromium towards Ammonium Hydroxide.—To a solution containing in 30 cc. 3 or 4 cc. HCl (1·12) and 250 mgrms. Cr as $CrCl_3$ freshly prepared by boiling K_2CrO_4 with concentrated HCl, was added NH_4OH (0·96)

* From the *Journal of the American Chemical Society*, xxx., No. 4.

until after shaking the odour was distinct. The mixture was divided into two parts; one part was filtered at once; to the other part 10 cc. NH_4OH (0·96) were added, and it was immediately filtered; the former had only a very faint pink colour, and on boiling not more than 0·5 mgrm. Cr precipitated as $Cr(OH)_3$; the latter was distinctly pink, and on boiling 2 to 3 mgrms. Cr precipitated as $Cr(OH)_3$. The experiment was repeated, except that an excess of 2 cc. NH_4OH was added after the odour of NH_4OH was distinct, and that in addition 5 grms. solid NH_4Cl were added to one-half of the mixture, and both portions were filtered at once; each filtrate was faintly pink, and on boiling that containing no excess of NH_4Cl there resulted a precipitate of $Cr(OH)_3$ estimated to contain 0·5 mgrm. Cr, while on boiling the other filtrate no precipitate separated, and the solution remained pink. The last experiment was repeated, except that the mixtures were allowed to stand twenty hours before filtering; the filtrate containing no excess of NH_4Cl was faintly pink, but did not contain more than 1 mgrm. Cr. The second filtrate was highly coloured, and on boiling 5 to 10 mgrms. Cr precipitated as $Cr(OH)_3$, but the precipitation was not quite complete. These results show that both NH_4OH and NH_4Cl increase the amount of the pink chromium compound formed, and therefore prove that this compound is a complex ammonia salt and not a chromite. For the proof that these solutions are unstable, even at room temperatures, see Herz (*Zeit. Anorg. Chem.*, 1902, xxxi., 357).

P. 51, N. 6: *Precipitation of Phosphates of Calcium, Barium, Magnesium, and Manganese by Ammonium Hydroxide.*—To solutions containing 2 mgrms. PO_4 as Na_2HPO_4 and 4 cc. HCl (1·12) in 30 cc., were added in separate experiments varying amounts of manganese, barium, and magnesium as chloride, and of calcium as nitrate. The solutions were then neutralised with NH_4OH (0·96) and about 2 cc. excess added, making 8 cc. in all, after which the mixtures were shaken and allowed to stand; 2 and 3 mgrms. Mn gave small precipitates after a minute or two, but 1 mgrm. gave no precipitate; 10 and 20 mgrms. Ca gave large precipitates at once, but 5 mgrms. gave no precipitate even in half-an-hour. 100 mgrms. Ba gave a large precipitate at once, and 50 mgrms. gave no precipitate in half-an-hour. One, 3, and 5 mgrms. Mg gave precipitates on shaking. The experiment was repeated with 10 mgrms. PO_4 and varying amounts of barium. Sixty mgrms. Ba gave a large precipitate at once, but 40 mgrms. gave no precipitate, or only a very small one, in half-an-hour. The experiment was repeated with 2 mgrms. Ca and varying amounts of phosphate; with 30 mgrms. PO_4 a precipitate was obtained at once, with 20 mgrms. after several minutes, and with 10 mgrms. no precipitate appeared in half-an-hour. On repeating the experiment with 1 mgrm. Ca a precipitate was obtained with 30 mgrms. PO_4 after a few minutes, but not with 20 mgrms.

P. 51, N. 7: *Solubility of the Borates of the Alkaline Earth Elements.*—500 mgrms. BO_2 as H_3BO_3 and 20 mgrms. Ca as chloride were dissolved in 4 cc. HCl (1·12) and 36 cc. water, and NH_4OH (0·96) were added until the mixture after shaking just smelled of it; no precipitate separated. The experiment was repeated with 200 mgrms. Ba as chloride; no precipitate separated. The experiment was repeated with 300 mgrms. Ba; a small precipitate formed, but it dissolved on adding a little concentrated NH_4Cl solution. The experiment was repeated with 500 mgrms. Mg as chloride; no precipitate resulted.

P. 51, N. 9: *Action of Ammonium Hydroxide on Uranyl Solutions.*—See Kern (*Journ. Am. Chem. Soc.*, 1901, xxiii., 701). One and 3 mgrms. U as $UO_2(NO_3)_2$ were dissolved in separate experiments in 20 cc. water, and a few drops NH_4OH (0·96) were added; no precipitate separated on standing, nor on boiling. A small quantity of solid $NaNO_3$ was added to the cold solutions; pale yellow precipitates separated at once, showing that the uranium had been present in the colloidal form. The experiment with 1 mgrm. U was repeated, except that a little NH_4Cl instead of $NaNO_3$ was added; a yellow precipitate separated.

P. 51, N. 9: *Uranyl Salts and Diuranates.*—See Dittrick (*Zeit. Phys. Chem.*, 1899, xxix., 449), Kern (*Journ. Am. Chem. Soc.*, 1901, xxiii., 686).

P. 51, N. 10: *Completeness of Precipitation of the Sulphides of the Iron Group.*—In each of the following experiments the quantity of the element given below was dissolved in 4 cc HCl (1·12) and 96 cc. water; to this solution in the cold were added 9 to 10 cc. NH_4OH (0·96), and then $(NH_4)_2S$ solution drop by drop until an excess was present. The mixtures were well shaken, and then filtered, generally through a double filter. The results were as follows:—With 5 mgrms. Mn as $MnCl_2$, a light coloured precipitate was formed at once; the filtrate was clear after two filtrations. With 0·5 mgrm. Mn as $MnCl_2$, the result was the same. With 0·25 mgrm. Mn as $MnCl_2$, the solution became turbid in two or three minutes. The filtrate in the first two experiments was evaporated almost to dryness; HNO_3 (1·42) was added; the mixture was evaporated to 5 cc., $KClO_3$ was added, and the mixture boiled; no precipitate of MnO_2 separated, showing that the precipitation of MnS had been complete.

With 1 mgrm. Zn as $Zn(NO_3)_2$, the mixture became turbid at once, and was readily filtered. With 0·5 mgrm. Zn, the result was the same. The filtrate in the first experiment was evaporated to 5 cc., made alkaline with NH_4OH and $(NH_4)_2S$ was added; only an insignificant turbidity appeared, showing that the precipitation of ZnS was practically complete.

With 0·5 mgrm. Co as $Co(NO_3)_2$, a black precipitate formed at once, which was readily filtered off. With 0·1 mgrm. Co, the solution became dark coloured at once.

With 0·2 mgrm. Fe as $FeSO_4$, the solution became dark coloured at once, and the precipitate was easily filtered off. With 0·5 mgrm. Fe as $FeSO_4$, the result was the same. The filtrate was evaporated to 5 cc.; NH_4OH and $(NH_4)_2S$ were added; the solution remained colourless.

With 0·3, 0·5, and 1·0 mgrm. Tl as Tl_2SO_4, the solutions became dark brown at once, and yielded clear filtrates, which when evaporated almost to dryness and tested for thallium by *P. 65*d*, gave no precipitate of TlI.

With 0·5 and 1·0 mgrm. U as $UO_2(NO_3)_2$, distinct flocculent precipitates could be seen after the addition of $(NH_4)_2S$; the filtrates were clear, and the precipitate, when collected on the filter, was yellow in colour. With 0·3 mgrm. U as $UO_2(NO_3)_2$, a slight coloration was seen on the filter, but the precipitate could scarcely be seen before filtration. With 5 mgrms. U as $UO_2(NO_3)_2$, the result was the same. The filtrate was evaporated almost to dryness, and was tested for uranium by *P. 58*d* with $K_4Fe(CN)_6$; no brown coloration was observed. The last experiment was repeated, except that the filtrate was evaporated to 5 cc. and NH_4OH and $(NH_4)_2S$ added; no precipitate formed, showing that the precipitation as sulphide in 100 cc. had been complete.

Nature of the Uranium Precipitate produced by Ammonium Sulphide.—Twenty mgrms. U as $UO_2(NO_3)_2$ were dissolved in 4 cc. HCl (1·12) and 96 cc. water, about 9 cc. NH_4OH were added, and $(NH_4)_2S$ drop by drop in the cold, until a distinct excess was present. The precipitate was flocculent and had a bright yellow colour. After two hours it was light brown, and in six hours dark brown in colour. The experiment was repeated, except that a much larger excess of $(NH_4)_2S$ was added; the precipitate darkened more rapidly. It is evident that $(NH_4)_2U_2O_7$ is first precipitated contrary to the statements in some text-books, and that the conversion of this substance into UO_2S takes place slowly.

The Existence of Ferric Sulphide (Fe_2S_3).—That Fe_2S_3 is formed when $(NH_4)_2S$ is added to suspension of $Fe(OH)_3$ in dilute NH_4OH has been proved by Stokes (*Journ. Am. Chem. Soc.*, 1907), xxix., 304. When, however, an acid solution is first saturated with H_2S and then made alkaline with NH_4OH, FeS and not Fe_2S_3 is formed.

P. 51, N. 11: *Dark Colour of Sulphide Precipitate as Evidence of Iron, Nickel, or Cobalt.*—To solutions containing 500 mgrms. Zn. as nitrate, 4 cc. HCl (1·12) and

30 cc. H_2O were added in separate experiments 1 and 2 mgrms. Ni as nitrate, 1 and 2 mgrms. Co as nitrate, 1 mgrm. Fe as $FeSO_4$, and 1 mgrm. Fe as $FeCl_3$. The mixtures were neutralised with NH_4OH (0·96) and 3 or 4 cc. excess added, making 10 cc. in all. A large white precipitate of $Zn(OH)_2$ remained which was estimated to contain at least 100 mgrms. Zn. Colourless $(NH_4)_2S$ was then added as described in P. 51, and the colour of the precipitate was compared with that obtained with 500 mgrms. pure zinc; the precipitates containing 1 mgrm. Fe were nearly black with a greenish tinge; those containing 2 mgrms. Ni and Co were much darker than the pure ZnS, but those with 1 mgrm. Ni and Co were only very slightly darker. The experiment was repeated except that 4 cc. more $(NH_4)OH$ were added in order to dissolve the $Zn(OH)_2$; the results were substantially the same. A solution containing 500 mgrms. Ca and 1 mgrm. Ni as nitrates, 1 grm. PO_4 as $(NH_4)_2HPO_4$, 4 cc. HCl (1·12) and 35 cc. H_2O was made alkaline with NH_4OH (0·96) and 1 cc. colourless $(NH_4)_2S$ was added: the large white precipitate of phosphate became dark coloured as soon as the sulphide was added.

P. 51, N. 12: *Behaviour of Nickel towards Ammonium Monosulphide and Polysulphide.*—See Lecrenier (*Chem. Zeit.*, 1889, xiii., 431, 449), Anthony and Magri (*Gazz. Chim. Ital.*, 1901, xxxi., II., 265). By boiling the brown solution in the absence of air the last-named authors have prepared NiS_4. The composition of the brown solution is unknown; it may be ammonium sulpho-nickelate, $(NH_4)_2NiS_{2+x}$, or colloidal nickel persulphide.

That in absence of air nickel is completely precipitated as NiS and the filtrate is colourless, thus proving that the brown solution is due to the presence of polysulphide, has been shown by Lecrenier (*Chem. Zeit.*, 1889, xiii., 431, 449) and Villiers (*Comptes Rendus*, 1894, cxix., 1263). The presence of NH_4OH tends to prevent the precipitation of NiS, and it is possible to obtain colourless (or bluish) solutions, containing a small excess both of $(NH_4)_2S$ and of nickel. In the presence of air we have found it almost impossible, when working with large amounts of a pure nickel salt, to prevent some nickel from passing into the filtrate, giving a brown solution. The amount of nickel in the filtrate increased with the excess of ammonium sulphide used and with the length of exposure to the air.

Some of the brown solutions obtained in these experiments were boiled in small flasks for three to ten minutes, and then filtered; in each case the filtrate was colourless after a single filtration.

Precipitation of Nickel in Ammoniacal Solution by Hydrogen Sulphide.—In several experiments 500 mgrms. Ni as $Ni(NO_3)_2$ were dissolved in 30 cc. water and 4 cc. HCl (1·12); NH_4OH (0·96) was added until the odour could be detected after shaking and then 3 cc. more, and H_2S was led into the mixture for fifteen minutes; the precipitates were always granular, and the filtrates clear and colourless; when the precipitates were washed with water containing either H_2S or a little $(NH_4)_2S$ the wash water was invariably clear.

(To be continued).

NOTICES OF BOOKS.

Forty-fourth Annual Report on Alkali, &c., Works. By the Chief Inspector. London: Eyre and Spottiswoode, Ltd. 1908.

This annual report contains a condensed account of the important work published by Dr. Raschig during 1907 on the nature of the reactions which occur in the lead chamber process, and also a full report is given of the investigations of Mr. Linder on the use of "Dolly Cream" dye as a selective indicator for the detection of certain acids in gaseous mixtures. By means of these investigations the exact uses and limitations of this indicator have been defined. The work of Prof. Percy Frankland and Mr. H. Silvester on the bacterial treatment of spent ammoniacal liquors is also summarised.

Das Erdöl, seine Verarbeitung und Verwendung. ("Petroleum, its Preparation and Applications"). By Dr. Richard Kissling. Halle-a-S.: Wilhelm Knapp. 1908.

This is one of the best of the smaller books on petroleum which has come under our notice of late years. It is intended principally for those chemists who want to read through an introductory survey before proceeding to the study of larger treatises, and for this purpose they will find it excellent. The author has endeavoured to present a many-sided view of the subject, at the same time carefully avoiding any excess of detail, and throwing the information into the most concise form possible. The matter is so well chosen that the reader will have nothing to unlearn when he passes on to more detailed work, and, moreover, all that he has learnt will form a ground-work upon which further knowledge can very readily be based. The distribution and supply, the chemical nature, preparation, and uses of petroleum are all discussed as far as possible in general terms, and typical methods and processes are always chosen for consideration. The bearings of theory upon practice receive careful attention, and all points of special practical signification are given the prominence which their importance demands. A thoroughly systematic and well-arranged treatment of each division of the subject accounts for the large amount of matter contained in a small space, and every branch of the petroleum industry is discussed in short accounts in which no essential points are overlooked.

Laboratoriumsbuch für die Industrie der Riechstoffe. ("Laboratory Book for the Perfumery Industry"). By Dr. Oskar Simon. Halle-a-S.: Wilhelm Knapp. 1908.

The first part of this book contains a description of those methods of analysis which may most conveniently be applied to identify, or test the purity of, the most important perfumes. Both physical and chemical methods of investigation are included, and the experimental directions are full enough to enable anyone who has had some general training in practical chemistry to perform the tests without further assistance and without much difficulty. The separation of hydrocarbons from ethereal oils and their identification is a subject which is rather scantily treated, some important hydrocarbons, as, for instance, thuyene and styrol, being omitted. In the second part of the book short accounts are given of the most common perfumes; their origin is discussed, and their physical constants are enumerated; some notes are also added on modifications of the general methods of analyses which may conveniently be used in special cases.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvii., No. 13, September 28, 1908.

Relative Stability of the Cyclic Poly-carbon Groups. — Louis Henry. — Dehydrating agents act on dimethylisopropylcarbinol, $(H_3C)_2=C-CH=(CH_3)_2$ (with OH), giving the two unsaturated isomeric hydrocarbons—tetra-

methylethylene, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!C=C\!<\!\begin{matrix}CH_3\\CH_3\end{matrix}$, and methylisopropylethylene, $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\!-\!\underset{CH_3}{\overset{|}{C}}=CH_2$, in the proportion of three parts of the former to one of the latter. The investigation of the corresponding tertiary albohol containing the cyclic group $\begin{matrix}H_2C\\|\\H_2C\end{matrix}\!>\!CH,-$

$$\begin{matrix}H_2C\\|\\H_2C\end{matrix}\!>\!CH\!-\!\underset{OH}{\overset{|}{CH}}\!<\!\begin{matrix}CH_3\\CH_3,\end{matrix}$$

shows that the group $\begin{matrix}H_2C\\|\\H_2C\end{matrix}\!>\!CH$ is relatively stable, and the elimination of H—OH occurs at the expense of the system $-\underset{OH}{\overset{|}{C}}\!<\!\begin{matrix}CH_3\\CH_3.\end{matrix}$

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xli., No. 13, 1908.

Preparation of Hydrazoic Acid.—Johannes Thiele.—The conversion of hydrazine into hydrazoic acid by nitrous acid, by oxidation either alone or in presence of hydroxylamine, or by the action of nitrogen chloride, gives only small yields. But if ethyl nitrite is allowed to act on hydrazine in presence of alkali, good yields of sodium nitride are obtained, especially if excess of nitrite is used. Ethyl nitrite is not saponified by alkali in the cold, and the free hydrazoic acid can be obtained in aqueous solution by allowing hydrazine sulphate to react with ethyl nitrite in presence of caustic soda. Sodium nitride can also be obtained by heating hydrazine hydrate with sodium nitrite in aqueous solution. The reaction takes place slowly, and is incomplete; it is accelerated by the presence of some hydrazine sulphate, or by large quantities of sodium hydroxide.

Reduction of Nitro-compounds with Zinc Dust and Acetic Acid.—Gustav Heller.—When different ortho-nitro compounds are subjected to the same reduction process with zinc dust and acetic acid, the results obtained vary apparently irregularly, but the residue in the ortho-position appears to facilitate the reaction. Thus, ortho-nitromandelic acid nitrile is very readily reduced at 0°, while under the same conditions nitrobenzene is almost unchanged. Phenylhydroxylamine is formed, for the aqueous solution gives phenylazohydroxylanilide with diazobenzene chloride. *o*-Nitrobenzaldehyde gives *o*-amino-benzaldehyde and anthranil. From the products of the reduction of *o*-nitrobenzoic acid, benzidine dicarboxylic acid and azoxybenzoic acid can be isolated.

Molecular Weight and Hydrate of Hypophosphoric Acid.—Arthur Rosenheim and Max Pritze.—Hypophosphoric acid esters (ethyl and methyl), and pyrophosphoric acid ester were prepared by the action of alkyl iodide on silver hypo- or pyrophosphate, and their molecular weights were determined by the boiling-point method. The pyrophosphoric acid esters gave values which agreed very closely with the molecular weights of the substances of formulæ $(CH_3)_4P_2O_7$, $(C_2H_5)_4P_2O_7$, while with the same solvents the corresponding hypophosphoric esters give numbers which point to the simple formula H_2PO_3 for the acid. When a solution of free hypophosphoric acid is allowed to crystallise over sulphuric acid *in vacuo*, tabular transparent crystals are formed. They melt at 62°, and the analysis of them shows that they are the monohydrate, $H_2PO_3.H_2O$. This monohydrate is stable between 0° and 60°.

New Synthesis of Aromatic Carboxylic Acids from Hydrocarbons.—Paul Schorigin.—When carbon dioxide acts on a mixture of sodium and mercury alkyl in benzene solution a fatty acid and benzoic acid are formed. Apparently a sodium alkyl is formed as an intermediate product, the reaction occurring in phases as follows:—

$$\text{I.}\quad Hg(C_6H_5)_2 + 2Na = Hg + 2NaC_2H_5.$$
$$\text{II.}\quad C_6H_6 + NaC_2H_5 \quad NaC_6H_5 + C_2H_6.$$
$$\text{III.}\quad C_6H_5Na + CO_2 = C_6H_5.COONa.$$

Mercury diethyl can be replaced by zinc diethyl in this reaction. When this reaction was extended to other aromatic hydrocarbons it might be expected that the sodium and carbon dioxide would enter the benzene nucleus, but, on the contrary, it is found that when mercury diethyl is used the acids with the carboxyl in the side-chain result. Apparently this new method of synthesing carboxylic acid can only be applied to the benzene derivatives. The reaction is caused by the great lability of sodium alkyls.

Triphenylstibine Sulphide.—Ludwig Kaufmann.—The cautious introduction of sulphuretted hydrogen into an alcoholic ammoniacal solution of triphenyl stibine leads to the separation of white crystalline needles of triphenylstibine sulphide; further introduction of sulphuretted hydrogen turns the liquid an intense yellowish red, and from this liquid triphenylstibine can be isolated. In all probability the hydroxide, $(C_6H_5)_3Sb(OH)_2$, is formed as an intermediate product, and then decomposed quantitatively according to the equation $(C_6H_5)_3Sb(OH)_2 + H_2S = (C_6H_5)_3SbS + 2H_2O$. When the sulphide is subjected to the action of sulphuretted hydrogen it dissolves, and a yellow coloration is produced; this is due to the antimony compound formed from the sulphide, and dissolved in alcohol. It is possible that on solution a sulpho-salt or a derivative of tetravalent sulphur is formed, $(C_6H_5)_3Sb\!<\!\begin{matrix}S.NH_4\\SH\end{matrix}$ or $(C_6H_5)_3Sb : S : S\!<\!\begin{matrix}NH_4\\H\end{matrix}$. Whatever the nature of the intermediate substance, it is very labile and readily undergoes decomposition. If a solution of the sulphide in alcoholic ammonium sulphhide is prepared in such a way that an excess of ammonium sulphide is avoided, and the solution is filtered and allowed to stand, the colourless liquid gives only triphenylstibine when it evaporates in a vacuum desiccator.

Action of Magnesium Organic Compounds on Arsenious Acid.—Franz Sachs and Hans Kantorowicz.—Although arsenious acid is practically insoluble in ether, when it is finely powdered and introduced into Grignard's solution a reaction occurs; heat is evolved, and the acid disappears. The reaction is complicated, and, according to the organo-metallic components, different final products are obtained. Thus, in the cold, diphenylarsenic oxide is obtained when phenyl magnesium bromide is used, while the product is triphenylarsine when the temperature is raised, $C_6H_4(CH_3)$. MgBr gives only tritoluylarsine, but benzyl magnesium chloride gives a compound which is probably $(C_6H_5.CH_2)_2As.OH + H_2O$.

MEETINGS FOR THE WEEK.

MONDAY, Nov. 2nd.—Royal Institution, 5. General Monthly Meeting.
Society of Chemical Industry, 8. "Chemical Industry in Relation to Agriculture," by A. Frank.

THURSDAY, 5th.—Chemical, 8.30. "Direct Union of Carbon and Hydrogen," by W. A. Bone and H. F. Coward. "Relation between Absorption Spectra and Chemical Constitution—Part XI., Some Aromatic Hydrocarbons," by E. C. C. Baly and W. B Tuck. "Organic Derivatives of Silicon—Part VII., Synthesis of *d*-Sulphobenzylethylisobutylsilicyl Oxide," by B. D. W. Luff and F. S. Kipping. "Chlorine Derivatives of Pyridine—Part IX., Preparation and Orientation of the Dichloropyridine M. p. 66 70°; Part X., Orientation of the Trichloropyridine M. p. 49—50°" and "Chlorination of the Methyl Derivatives of Pyridine—2-Methyl Pyridine (Part II.)," by W. J. Sell. "The Triazo-group Part V., Resolution of α-Triazopropionic Acid; Part VI., Triazoethyl Alcohol and Triazoacetaldehyde," by M. O. Forster and H. E. Fierz.

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THE DECOMPOSITION OF YTTERBIUM INTO ITS ELEMENTS.*

By C. AUER von WELSBACH.

The Method of Separation.

On page 11 of my article which appeared last year, "On the Elements of the Ytterbium Group," Part I., I mentioned that the last member of all ytterbium fractions from the purified final mother-liquors of the principal series was a fraction the spark spectrum of which showed striking differences from the normal ytterbium spectrum. For example, the 4-line group in the green ($\lambda = 5353{\cdot}0$, $5347{\cdot}4$, $5345{\cdot}9$, $5335{\cdot}2$), which is so characteristic of ytterbium, was much weakened; other lines (mostly fainter) were altogether missing.

This peculiar spectrum, which appeared very clearly, especially if the luminous intensity of the spark was feeble, gradually disappeared in the fractions following.

As the spark spectrum of the end fraction consisted exclusively of ytterbium lines, from the changes of intensity which the lines had undergone, it must be concluded that one constituent of ytterbium had accumulated in the more soluble fractions, so that ytterbium cannot be an elementary substance.

Other observations also pointed to the same conclusion, long before the discovery of this spectral phenomenon. For instance, it was very remarkable that the separation process for erbium and thulium on the one hand, and ytterbium on the other, was effected more slowly the longer it was continued. While at first after a few series colourless ytterbium salts giving no absorption spectrum could be obtained, this became gradually more difficult, although the ytterbium fractions put aside as pure remained almost unchanged in amount. If it was proved that on fractionating the double ammonium oxalates one constituent of the ytterbium—for the present I shall call it Yb I.—had accumulated in the more soluble fractions, naturally after a correspondingly lengthy fractionation this constituent must have decreased in the difficultly soluble double salts, and consequently another constituent of ytterbium must have increased.

But these difficultly soluble double salts are those fractions containing little erbium which occur between the colourless ytterbium fractions and those richer in erbium. As solid salts all these fractions show, besides the Tu bands, that remarkable spectrum which is quite different from the absorption spectrum of pure erbium salts, and which I called the spectrum Er γ in the article mentioned above.

I first set to work on these fractions. I added to them later all those erbium fractions in which the holmium lines could no longer be detected.

The fractionation was performed as before. As after fifty series it was continually becoming more difficult to get quite colourless fractions, and the number of the fractions of the series was continually increasing, I removed the very faintly pink-tinged fractions which gave the above-mentioned Er γ spectrum, and put them together in several collective fractions.

The mother-liquors of these series were evaporated, and gave small quantities of perfectly colourless fractions which were added to the ytterbium fractions previously obtained.

After the seventy-fifth series I was putting aside salts which were more strongly pink coloured than those removed before, and which all showed to a slight extent the characteristic bands of the erbium spectrum, besides the spectrum Er γ.

* *Monatshefte für Chemie*, February, 1908.

The mother-liquors of these series were no longer put with the others. They finally gave, after repeated evaporation, a fraction which hardly showed the erbium spectrum, Mother-liquor I.

Putting aside the middle pure erbium fractions, to which I shall not allude further in this article, I allowed the crystallisation process to go on to the end. These last series gave, finally, a final Mother-liquor II. and a large quantity of faintly pink-coloured salts which all gave the spectrum Er γ.

Mother-liquor I., when precipitated with nitric acid, gave an almost white oxalate. It contains chiefly ytterbium.

Mother-liquor II. gave a very pale pink oxalate.

In all these fractions a small amount of elements allied to tin was present. I shall deal in a special article with these interesting substances which occur in all minerals containing the elements of the Yb group.

In the spark spectrum of the pure oxide prepared from the oxalate of Mother-liquor II. there appeared very clearly the countepart of the spectrum described at the beginning of this article. All ytterbium lines which appeared paler in that spectrum were brighter in this spectrum, especially the 4-line group in the green. The spectrum of this second ytterbium constituent—it may provisionally be called Yb II.—appeared still more clearly in the faintly pink-coloured fractions which followed Mother-liquor II. In the spectra of these preparations the lines which appear so brilliant in the spectrum, described at the beginning of this article, can now hardly be seen.

As these spectra contained only the lines of Yb II., besides some erbium lines, it may be concluded that the substance causing the pink coloration of these fractions either possesses no sensitive spark spectrum, or else is present in traces only. The first assumption suggests erbium. The spectrum of this substance is not specially bright in the visible part, although it contains many lines. Since, on the other hand, the substance giving the spectrum Er γ cannot be appreciably increased in the fractions, it may be assumed that this special spectrum, which has so often given rise to mistakes, is a variation of the erbium spectrum.

When I dissolved by boiling a mixture of ten parts of the purest ytterbium-ammonium oxalate and one part of the purest erbium ammonium oxalate in a solution containing as little ammonium oxalate as possible, and then allowed it to crystallise quickly, a double salt was formed which did not differ appreciably in colour nor in absorption spectrum from the fractions in question.

For completeness sake it must be mentioned that the spectra of all fractions containing a little erbium also showed clearly the absorption bands ascribed to thulium.

By the experiments just described it was shown that all faintly pink-coloured fractions contained about ten times more Yb II. than erbium. The spectrum Er γ was henceforward employed as a convenient indicator of the amount of ytterbium in the fractions.

Owing to the high percentage of Yb II. in the faintly pink-coloured fractions, it occurred to me to attempt the separation of this constituent of ytterbium by the basic nitrate method—a method which has proved effectual for the preparation of ytterbium.

After a preliminary experiment with a little pure salt had demonstrated the applicability of this method, I applied it to these fractions.

As I have already described the exact process in my earlier articles, I shall here report shortly on the results only. At first the separation of the constituents occurred in the normal way, but as soon as the amount of erbium had sunk below about $\frac{1}{2}$ per cent the separation became more difficult, so that it was only possible to get perfectly colourless erbium-free products by repeated fractionations. This somewhat negative result shows that the separation by means of the double ammonium oxalates is not only the more convenient but also the far better method.

I now arranged the fractions containing the ytterbium

elements into a new series. This was rather difficult, because the preparations came from different stages in the separation process, and contained very different amounts. I first got the above-mentioned faintly pink-coloured collective fractions into a series which consisted of ten fractions. At the head of these I placed those fractions which I had prepared from the mother-liquor of the basic salts. At the end came some other preparations of the last series containing much more erbium, so that this new series consisted of about sixteen members. The separation process then began again. As it went on I interpolated in the series the other ytterbium fractions of the principal series. Some of them gave no trace of absorption bands in the spectrum, but others showed them just plainly enough to be recognised. I shall henceforward denote the elements giving these absorption bands collectively as "erbium." Most fractions contained a large excess of ammonium oxalate, much more than was necessary to dissolve the salt on warming.

This excess must first be removed, because it would make the separation process from a hot solution difficult. For this purpose I prepared a solution of the mixture of salts saturated at about 90°, and then let it crystallise in a thermostat at 60°. After about twelve hours the solution was rapidly poured off from the ammonium oxalate separated, which had formed a crystalline mass adhering rather closely to the dish, into a previously warmed dish. By repeated crystallisations at about 30° C., it was easily possible to separate the ammonium oxalate nearly pure. In the liquor poured off from the crystals the other fractions were dissolved, treated in the way described above, and so on, until all were in solution in different portions. I kept these solutions more concentrated the more impure they were.

The separation of the first fractions was always performed at about 50° C. As soon as the amount of erbium had fallen below ⅓ per cent I let the liquors crystallise at room temperature. Corresponding fractions were put together and united to form a new series.

The mother-liquors arising from this series were repeatedly concentrated fractionally. The mother-liquors finally obtained, in which, besides rare earths, other impurities had accumulated, arising partly from the water used, were carefully precipitated with nitric acid. The precipitate consisting of earth oxalates and acid ammonium oxalate was filtered off, washed with cold water containing some oxalic acid, then suspended in water, and dissolved by heating, with the addition of a little ammonia. By putting together the corresponding fractions a new series was finally formed.

As the separation process was continued gradually the final members of the other series could be added to the new fractions, until, putting aside the faintly pink-coloured first members, all the fractions could be united in a single series.

This series contained nearly half a kilogrm. of ytterbium oxide.

It would be very tedious and wearisome if I were to give a detailed description of the subsequent separation process. I shall therefore only shortly allude to the most important steps in the process.

After the tenth series had been formed I put aside the crystal aggregate of the first fractions, and repeated this in almost every new series. Finally, I had forty crystalline fractions and a larger quantity of final mother-liquors as collective fractions. The first ten fractions amounted to about two-thirds of the total quantity. The first showed a still recognisable pink coloration, but all the rest were perfectly white, and gave no visible absorption spectrum, even with a deep layer. The spark spectrum of the first fractions contained only the lines of Yb II. In the next fractions the most intense lines of Yb I. could be detected. Towards the middle both spectra appeared strongly. The final fractions gave a brilliant spectrum of the second element, in which, however, the lines of the first element were still present. Even the oxide of the final mother-liquor gave with a strong spark the typical lines of Yb II. Even though the separation, in spite of every care, could not be regarded as complete, it seemed to me to be established beyond doubt that the preparation in the pure state of the two elements was at least within the bounds of possibility.

As from various experiments I had performed with the final mother-liquor, I had come to the conclusion that certain impurities, which could be detected in the liquor, had hindered the course of the separation. I next prepared the earth oxalate in the pure state. Nitric acid was added to the liquor till the tetracid ammonium oxalate was formed, when it was left to clear; the precipitate was afterwards drawn off and washed. The liquids were evaporated and ignited. The incombustible residue contained, besides much silicic acid, some alumina, a little iron, a trace of uranium, Cu, K, Na, &c. Also a small amount of ytterbium elements could be detected in it.

The earth oxalate precipitate was ignited. It gave about 8 grms. of oxide. This was dissolved in nitric acid, the clear liquid was evaporated, and the nitrate was cautiously fused till oxides of nitrogen began to appear. When cold the melt was turbid. When a little water was added, and it was warmed, it dissolved to a turbid liquid. On addition of some more water and boiling a white basic nitrate separated. After some time this precipitate was drawn off and dissolved in nitric acid. Sulphuretted hydrogen produced only a very small precipitate in the faintly acid solution. The filtrate was similarly precipitated with sodium thiosulphate. As this first precipitate showed the ytterbium elements in the spark spectrum it was again dissolved in hydrochloric acid, and cautiously re-precipitated with thiosulphate. This precipitate, which was small in proportion to the quantity used, consisted of almost pure thorium salt, as shown by spectral analysis.

In the principal quantity of the nitrate solution sulphuretted hydrogen produced only an almost inappreciable turbidity. From the mother-liquor of the thiosulphate precipitate the hydrates were next prepared, then they were dissolved in nitric acid, and added to the principal quantity. The earths contained in the nitrate solution I now subjected to other separation processes which seemed suitable for the separation of Yb I. But I was not successful. The small quantity of Yb II. which this preparation still contains is not in the least degree affected.

So then I returned to the original method of separation. As I had already observed that the separation is easier the less supersaturated the solution is, I now allowed the mother-liquor always to stand eight days over the crystals which had first separated. Repeated spectral examinations showed that the separation was satisfactorily effected. After repeated evaporation only a small quantity of mother-liquor was finally obtained; the oxides from it in the pure state gave in the visible part with an ordinary spark only the spectrum Yb I. The brightest lines of Yb II. could only be seen with a very strong spark, and even then there were only indications of them.

As I intended to repeat the separation processes later in order to obtain larger quantities of Yb I. I contented myself at first with only a few series. The final mother-liquor of the second and third series gave a product approximately resembling the first mother-liquor.

In order to prove whether there was another rare earth or another element between Yb I. and Yb II. I examined fractions 11, 12, and 13 thoroughly. These fractions contained about 100 grms. of oxide. With a layer of 60 mm. the colourless concentrated nitrate solution showed an indication of an absorption band in the red. However, this totally disappeared if the absorbing layer was rather less. The oxide of this fraction was white, and gave no flame spectrum. The spark spectrum was like that of pure ytterbium.

Sulphuretted hydrogen produced no precipitate, nor potassium sulphate, which proved that the sulphide forming elements were not present. The pure nitrate solution was finally again precipitated with acid ammonium oxalate, the

oxalate dissolved in ammonium oxalate with the addition of ammonia, and allowed to crystallise.

To prepare the element Yb II. in the pure state I made a new series from fractions 1 to 10 of the last series, and from the products obtained from the second working up process just described.

From some members of this series ammonium oxalate was removed, because they contained more of it than was necessary to dissolve the double salt.

The solution of the crystal fractions was always effected on the water-bath. The mother-liquor of the final fraction of each series was put aside, and the first fraction of the series always taken up with water. I allowed all fractions to crystallise for forty-eight hours. As soon as the first fraction contained but little ammonium oxalate, or none at all, thus either did not dissolve freely in water or was quite insoluble, it was put aside. Thus I obtained after about thirty series ten fractions very rich in earths. The first showed both Er and Tu in the absorption spectrum. The fourth fraction was pure white, like all the subsequent ones. They no longer showed an Er absorption spectrum. The fifth gave an oxide, the fairly concentrated nitrate solution of which (0·5 grm. oxide in 1 cc.) was perfectly colourless. The solution in a layer of 30 mm. showed only a faint absorption band in the extreme red. This band ascribed to thulium was lost in the later fractions.

The spark spectrum of these fractions, even with a very strong spark, gave none of the characteristic lines of Yb I. in the visible part of the spectrum. Only the lines peculiar to Yb II. appeared.

Thus the purity of the preparation had reached the limits of sensibility given by ocular observation. I now turned to the methods of investigation which would be most sensitive in the present case, *i.e.*, photographing the ultra-violet part of the spectra.

The developed plates showed the spark lines with extraordinary sharpness. By direct comparison of the spectrograms it could be shown (of course disregarding the lines common to both elements) that neither Yb I. nor Yb II. was quite pure.

I therefore determined to repeat the separation processes. With Yb II. this seemed to be fairly promising. For I had obtained a fairly large amount of this substance, large enough to render a new separation series possible. But I decided not to continue the work with Yb I., on account of the small quantity at my disposal. After I had left this very tedious work for some time I arranged the fractions rich in Yb II. in a new series.

Unfortunately my labours were not attended with success. In spite of numerous repetitions of the crystallisation process, in spite of many alterations of the method of separation, I did not succeed in separating Yb II. from Yb I. completely. In the spectrograms the well-marked lines of Yb I. always appeared. So I gave up further separation experiments. In considering the purity of the preparations it must be remembered that by taking photographs of the spectra the sensitiveness of the test may be increased to almost any desired extent. With the most sensitive plates it depends only upon the time of exposure whether a line is strongly marked on the plate or not. But if it is remembered that some lines of the two new elements act so strongly on the photographic plate that even with a fairly weak spark an exposure lasting only one second is sufficient to photograph the line clearly, it may easily be understood that with an exposure of 200 seconds or more the elements which are so difficult to separate do not appear to be free from one another.

I intend to repeat the separation process described in this article with more material than I had at my disposal, partly so that I may provide other investigators with sufficiently pure specimens for further measurements, and partly to find out whether by pushing the fractionation still further Yb I. can be obtained in a much purer state. It will take six or eight years to complete this tedious task.

As may be seen from the following description of the spark spectra of the two new elements, neither Yb I. nor Yb II. seems to be able to be further decomposed by the means now at our disposal.

As the decomposition of ytterbium into two new elements has been proved experimentally beyond doubt, it will be best to use the name ytterbium in the future only as a collective name, and to give the new substances new names. I suggest the name—

Aldebaranium (symbol Ad)

for the element called in the first part of this article Yb II., and resembling thulium or erbium, and—

Cassiopeïum (symbol Cp)

for the second element, called Yb I. in this article, the last in the series of the rare earths.

As regards the chemical properties of the two elements I can state them very shortly. The reactions are those of ytterbium. Chemically they cannot be distinguished from one another by any reactions, however carefully carried out. They form only one oxide which is stable at a red heat; it is a sesquioxide. All salts are derived from this. They are colourless if the acid is not coloured.

The Atomic Weights.

The atomic weights of the elements are very close.

Determinations performed according to Bunsen's method gave :—

For Aldebaranium.

(O = 16).

Analysis.	Oxide.	Sulphate.	Atomic weight.
I.	0·4181	0·6730	172·98
II.	0·5984	0·9634	172·88
III.	0·6173	0·9939	172·85
		Mean Ad	172·90

For Cassiopeïum.

I.	0·3716	0·5967	174·25
II.	0·3086	0·4956	174·19
III.	0·4026	0·6465	174·24
		Mean Cp	174·23

The following notes on these determinations may be added :—

The oxide of Analysis I. of aldebaranium was derived from an oxalate which had been obtained by repeated precipitation from strong nitric acid solution.

The oxides of Analyses II. and III. of Ad, as well as the oxides of the analyses of Cp, were obtained from a nitrate solution containing much ammonium nitrate and free from CO_2, which was repeatedly precipitated with ammonia free from CO_2.

The accuracy of the atomic weight determinations of these elements, apart from the magnitude of the atomic weight, were also affected unfavourably by the fact that the sulphates of these elements, on ignition, are very unstable as compared with other elements.

Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 2nd instant, Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Viscount Ridley, Dr. William Hunter, and Mr. Andrew Bennie were elected Members. The Honorary Secretary reported the decease of the Rt. Hon. the Earl of Rosse, K.P., F.R.S., a Manager and Vice-President, of Professor Henri Becquerel, and Prof. E. Mascart, Hon. F.R.S., Honorary Members, and Resolutions of Condolence with the families were passed.

THERMO-CHEMICAL EQUIVALENCE AND THE THERMO-CHEMISTRY OF NITROGEN.

By J. C. THOMLINSON, B.Sc.

When I originally suggested, through the columns of the Chemical News, the numbers given for thermo-chemical equivalents of some of the elements, I was aware that other numbers might be obtained algebraically which would give results with equal approximation to those obtained by experiment.

I might quote one author on chemistry who says that "the prime object of the study (thermo-chemistry) is to obtain relative measurements of the chemical affinities inducing reactions," and state, further, that the behaviour of ozone and the oxides of nitrogen lead me to think that the numbers I gave might actually represent the thermal changes taking place.

Having stated my belief in this possibility, I venture the following structural formula for nitrogen pentoxide:—

Theoretically, a compound with this structure would have an approximate heat of formation 12·504 cals., the experimental heat of formation being 13·000 cals., and this for solid nitrogen pentoxide.

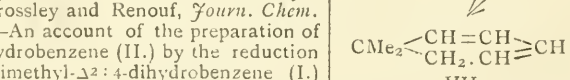
Another author I quote gives the heat of formation of nitrogen pentoxide (gaseous) zero, and solid as above.

As far as I can gather the gaseous pentoxide has not been isolated, and believing that the latent heats of liquids are, as a rule, less than that of water (80 cals.) from the liquid to solid state, I venture to think that this statement for gaseous nitrogen pentoxide need not detract from the correctness of the theoretical result I have given above.

Also for nitric acid, , I find the calculated heat of formation 45·447 cals., as against 41·600 cals.—the experimental value.

THE STUDY OF HYDRO-AROMATIC SUBSTANCES.*

1 : 1-Dimethyl-Δ^2 : 4-dihydrobenzene and 1 : 1-Dimethyl-Δ^2 : 5-dihydrobenzene (Crossley and Renouf, *Journ. Chem. Soc.*, 1908, xciii., 629).—An account of the preparation of 1 : 1-dimethyl-Δ^2 : 4-dihydrobenzene (II.) by the reduction of 3 : 5-dichloro-1 : 1-dimethyl-Δ^2 : 4-dihydrobenzene (I.) with sodium in moist ethereal solution appeared in 1902 (Crossley and Le Sueur, *Journ. Chem. Soc.*, 1902, lxxxi., 821).



I. II.

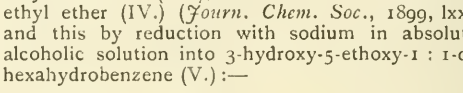
Shortly after the publication of this work, Harries and Antoni expressed doubt, not only as to the constitution, but also as to the composition of this hydrocarbon (*Annalen*, 1903, cccxxviii., 88). Their criticisms were, in part, answered at the time (*Ber.*, 1903, xxxvi., 2692), but it was considered desirable to try to prepare the substance by another method, in the hope that a comparison of the two specimens of the hydrocarbon would throw further light on the problem. This has now been done, with the result that the correctness of the earlier experiments and deductions are completely confirmed, allowing the following conclusions to be arrived at:—

1. The dimethyldihydrobenzene described by Crossley and Le Sueur is 1 : 1-dimethyl-Δ^2 : 4-dihydrobenzene, containing as impurity a very small amount of some oxygenated substance, probably a methoxy-compound.

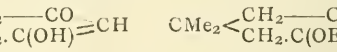
2. The hydrocarbon described in this report (dimethyldihydrobenzene, C. and R., see Note), and prepared by the elimination of two molecules of hydrogen bromide from dibromodimethylhexahydrobenzene, is a mixture, in approximately equal quantities, of pure 1 : 1-dimethyl-Δ^2 : 4-dihydrobenzene and pure 1 : 1-dimethyl-Δ^2 : 5-dihydrobenzene.

Note.—To avoid confusion as far as possible, the hydrocarbon described in this report, which is a mixture of pure 1 : 1-dimethyl-Δ^2 : 4-dihydrobenzene and of pure 1 : 1-dimethyl-Δ^2 : 5-dihydrobenzene, is referred to as dimethyldihydrobenzene (C. and R.), the 1 : 1-dimethyl-Δ^2 : 4-dihydrobenzene, prepared by Crossley and Le Sueur, as dimethyldihydrobenzene (C. and S.), and the supposed 1 : 1-dimethyl-Δ-^{2} : 5-dihydrobenzene of Harries and Antoni (*loc. cit.*) as dimethyldihydrobenzene (H. and A.).

The starting-point in the synthesis was again dimethyldihydroresorcin (III.), which was first converted into its ethyl ether (IV.) (*Journ. Chem. Soc.*, 1899, lxxv., 775), and this by reduction with sodium in absolute ethyl-alcoholic solution into 3-hydroxy-5-ethoxy-1 : 1-dimethylhexahydrobenzene (V.):—



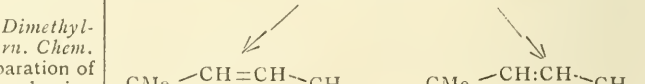
III. IV.



V.

The ethoxy-compound gives with fuming hydrobromic acid dibromodimethylhexahydrobenzene (VI.), which, when treaetd with quinoline, loses readily and completely two molecules of hydrogen bromide, with formation of dimethyldihydrobenzene, and this reaction takes place in two ways, giving rise to 1 : 1-dimethyl-Δ-^{2} : 4-dihydrobenzene (VII.), or to 1 : 1-dimethyl-Δ-^{2} : 5-dihydrobenzene (VIII.), in approximately equal amounts.

VI.



VII. VIII.

Table I. is a tabulated comparison of the properties of this hydrocarbon with those of the dimethyldihydrobenzene prepared by Crossley and Le Sueur. From this table the most important chemical properties of dimethyl-Δ^2 : 4-dihydrobenzene and dimethyl-Δ^2 : 5-dihydrobenzene would appear to be:—

1 : 1-Dimethyl-Δ^2 : 4-dihydrobenzene.	1 : 1-Dimethyl-Δ^2 : 5-dihydrobenzene.
Hydrobromide, $C_8H_{13}Br$, b. p. 83°/20 m.m.	Hydrobromide, $C_8H_{14}Br_2$, b. p. 137°/25 mm.
Nitrosochloride, m. p. 121°.	No nitrosochloride isolated.
Dibromide, $C_8H_{12}Br_2$, unstable liquid.	Tetrabromide, $C_8H_{12}Br_4$, m. p. 102°.
No nitro-derivatives obtainable.	Trinitro-*o*-xylenes, m. p. 71° and 115°.
Oxidation product, *as*-dimethylsuccinic acid.	Oxidation product, dimethylmalonic acid.

The criticisms of Harries and Antoni (*loc. cit.*) may then be replied to as follows:—

In the first place, these authors consider that the analyses given by Crossley and Le Sueur (*ibid.*) are midway be-

* Report of the Committee, consisting of Dr. E. Divers (Chairman), Prof. A. W. Crossley (Secretary), Prof. W. H. Perkin, Dr. M. O. Forster, and Dr. H. R. Le Sueur. Read before the British Association (Section B), Dublin Meeting, 1908.

Table I.

	Dimethyldihydrobenzenes.	
	C. and S.	C. and R.
Boiling-point	111°	111·2°
Sp. gr. at 15°/15° ..	0·8153	0·8147
Index of refraction ..	1·4548	1·4535
Molecular refraction .	60·217	60·251
Magnetic rotation ..	11·024	10·450
Colour with H_2SO_4..	Blood-red, turning to violet-purple.	Blood-red, turning to violet-purple.
Fuming HBr	Monohydrobromide, b. p. 90·5°/36 mm.	Monohydrobromide, b. p. 83°/20 m.m.; dihydrobromide, b. p. 137°/25 mm.
Bromine	Dibromide, unstable liquid.	Dibromide, unstable liquid; tetrabromide, m. p. 102°.
NOCl	Nitrosochloride, m. p. 121°.	Nitrosochloride, m. p. 121°.
Nitrating mixture ..	No definite product.	Trinitro-*o*-xylenes, m. p. 71° and 115°.
Oxidation products ..	*as*-Dimethylsuccinic acid.	*as*-Dimethylsuccinic acid; dimethylmalonic acid.
Oxidation products of monohydrobromide	*as*-Dimethylsuccinic acid; $\beta\beta$-dimethylglutaric acid; lactone of α-hydroxy-$\beta\beta$-dimethyl glutaric acid.	*as*-Dimethylsuccinic acid; $\beta\beta$-dimethylglutaric acid; lactone of α-hydroxy-$\beta\beta$-dimethyl-glutaric acid.

tween those for a dimethyldihydro- and a dimethyltetrahydro-benzene. The mean of the two analyses quoted gave C = 88·30 and H = 11·27, and it is obvious from the annexed comparison that the numbers do not lie midway between the calculated figures, the differences in those found and calculated for C_8H_{14} being very large, and the errors in the wrong direction; for, as a rule, carbon is found too low and hydrogen too high, and not *vice versâ*. Moreover, if any appreciable quantity of dimethyltetrahydrobenzene had been present it could hardly have escaped detection, as on oxidation it would have yielded $\beta\beta$-dimethyladipic acid, which presents no difficulty of isolation or identification.

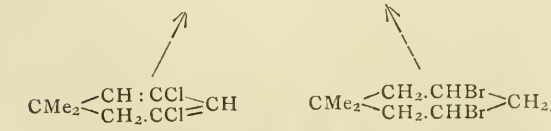
Difference.	Calculated. C_8H_{14}.	Found.	Calculated. C_8H_{12}.	Difference.
+1·03	87·27	C = 88·30	88·88	−0·58
−1·46	12·73	H = 11·27	11·11	+0·16

If the above-quoted figures for dimethyldihydrobenzene (C. and S.) are examined, it will be found that they add up to 99·57; and it is considered most probable that the discrepancy is due to oxygen present in the form of traces of a methoxy-compound.

Another suggestion made by Harries and Antoni is that dimethyldihydrobenzene (C. and S.) is not a true dihydrobenzene, but contains a trimethylene ring as represented in Formula IX.:—

IX.

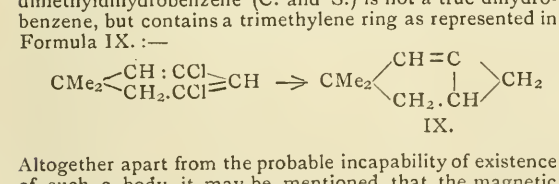
Altogether apart from the probable incapability of existence of such a body, it may be mentioned that the magnetic rotation of the hydrocarbon would have at once proved the presence of a trimethylene ring, and, moreover, there is now evidence that the same dimethyldihydrobenzene is produced by the reduction of dichlorodimethyldihydrobenzene, and by the removal of the elements of hydrogen bromide from dibromodimethylhexahydrobenzene.



This can only be explained if the substance be designated 1 : 1-dimethyl-Δ^2 : 4-dihydrobenzene, and hence the possibillty of a trimethylene ring being present in the hydrocarbon is precluded.

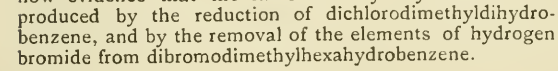
The whole question is further complicated by the fact that Harries and Antoni prepared a hydrocarbon, which they believed to be 1 : 1-dimethyl-Δ^2 : 5-dihydrobenzene also from dimethyldihydroresorcin as a starting-point; but, unfortunately, no information is given as to any derivatives which would enable a comparison to be made with the hydrocarbon having that undoubted structure described in this report; and it would appear that the present evidence is insufficient definitely to establish the constitution of Harries and Antoni's hydrocarbon. The single piece of evidence on which the supposed constitution of this latter substance is based is oxidation, whereby oxalic, a succinic, and malonic acids were obtained, none of which bodies afford any direct proof that the hydrocarbon contained the *gem*-dimethyl group.

Nor is there any apparent reason for supposing that the elimination of ammonia from the cyclic diamine would take place in one way and one way only. Harries and Antoni have themselves shown that, when the phosphate of diaminohexahydrobenzene (X.) is submitted to dry distillation, ammonia is evolved in both of the possible directions, giving rise to a mixture of Δ^1 : 3-dihydrobenzene (XI.) and Δ^1 : 4-dihydrobenzene (XII.)—



XI. X. XII.

and they therefore conclude that "the *gem*-dimethyl group influences the position taken up by the double bonds"—



If this is so, why does it not influence the position of the double bonds when hydrogen bromide is eliminated from dibromodimethylhexahydrobenzene? For this is a

reaction strictly analogous to the reaction used by Harries and Antoni, and yet it takes place in both ways, giving rise to a mixture of the two possible hydrocarbons in equal

amounts. The presence of the *gem*-dimethyl group certainly does not exercise any apparent influence in this case, nor in the position of the double bond formed when 3-bromo-1:1-dimethylhexahydrobenzene loses the elements of hydrogen bromide (*Journ. Chem. Soc.*, 1906, xxxix., 1556).

Harries and Antoni state that 2 grms. of their dimethyldihydrobenzene gave, on treatment with a nitrating mixture, 0·6 grm. of trinitro-*m*-xylene, which might be regarded as a proof that dimethyldihydrobenzene (H. and A.) does not contain the *gem*-dimethyl group, for though many cases of the wandering of a methyl group in derivatives of *gem*-dimethyldihydroresorcin have been recorded (*Journ. Chem. Soc.*, 1904, lxxxv., 264; 1906, lxxxix., 875), no single instance has been observed in which a methyl group has wandered into anything but an ortho- position. Moreover, dimethyldihydrobenzene (C. and R.) undoubtedly contains dimethyl-$\Delta^{2:5}$-dihydrobenzene, and under the influence of a nitrating mixture it is this hydrocarbon which is converted into the two possible trinitro-*o*-xylenes.

(To be continued).

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

PART III.—ANALYSIS OF THE ALUMINIUM AND IRON GROUPS, INCLUDING BERYLLIUM, URANIUM, VANADIUM, TITANIUM, ZIRCONIUM, AND THALLIUM.

By ARTHUR A. NOYES, WILLIAM C. BRAY, and ELLWOOD B. SPEAR.

(Continued from p. 221).

Confirmatory Experiments and References (continued).

*P. 51*a*, N. 1: *Test for Vanadate with* H_2S *in Alkaline Solution.*—To separate solutions containing 3 grms. NH_4Cl and 5 cc. NH_4OH (0·90) in a volume of 110 cc. were added 0·1, 0·3, and 0·5 mgrm. V as vanadate, and the mixtures were saturated with H_2S: in the experiments with 0·3 and 0·5 mgrm. V the solutions quickly became dark yellow, then reddish yellow, and finally pink; in that with 0·1 mgrm. V the solution finally became faintly pink, but the test was a poor one. Therefore, the limit of detectability under these conditions is 0·1 to 0·2 mgrm.

The experiment with 0·5 mgrm. V was repeated except that, instead of 5 cc. NH_4OH (0·90), 1, 2·5, and 10 cc. respectively were used: with 1 cc. and with 2·5 cc. NH_4OH the pink colour was scarcely noticeable; with 10 cc. a good colour was obtained as with 5 cc. NH_4OH, but only after passing in H_2S for a longer time. These experiments show that a fairly large excess of NH_4OH is necessary.

20 mgrms. V as Na_3VO_4 were added to 20 cc. NH_4OH (0·96) and H_2S passed in: the colour quickly became brown and slowly turned red, becoming after five or six minutes a deep cherry-red. The solution was divided into two parts. To the first was added an equal volume of water: the red colour disappeared in two or three minutes, but appeared again on re-saturating with H_2S. To the second part of the red solution was added an equal volume of NH_4OH (0·96): the colour faded slowly (in four or five minutes) but reappeared on passing in H_2S. These experiments show that the solution must be saturated with H_2S.

1 mgrm. V as Na_3VO_4 was dissolved (*a*) in 20 cc. NH_4OH (0·90), (*b*) in 20 cc. NH_4OH (0·96), (*c*) in 5 cc. NH_4OH (0·96) and 15 cc. water, (*d*) in 2 cc. NH_4OH (0·96) and 38 cc. water, (*e*) in 2 cc. NH_4OH (0·96) and 98 cc. water. Each solution was saturated with H_2S: a good colour was obtained in every case, showing that in the absence of ammonium salts the test may be obtained in any concentration of NH_4OH.

A solution containing 1 mgrm. V as Na_3VO_4 and 3 cc. HNO_3 (1·42) in 10 cc. was neutralised with NH_4OH (0·90) and 1 or 2 cc. in excess added: on saturating with H_2S a very faint colour was obtained. The experiment was repeated, except that the acid solution was first evaporated to dryness and ignited: a very good test was obtained, showing that the presence of ammonium salts interferes with test for vanadium.

0·5 mgrm. V as Na_3VO_4 was added to some HCl (1·20) and the mixture was evaporated twice nearly to dryness to reduce the vanadic acid to hypovanadic acid; 4 cc. HCl (1·12) were added and 96 cc. water; the mixture was neutralised with NH_4OH (0·90), an excess of 5 cc. was added, and H_2S passed in for ten to fifteen minutes: the solution darkened quickly, became reddish yellow, and finally pink; the colour was exactly the same as in the experiment described above with 0·5 mgrm. V as Na_3VO_4. The experiment was repeated with 25 mgrms. V, which was reduced to hypovanadic acid by long continued treatment of the hot solution with H_2S: the solution darkened and then became deep red very quickly; the colour was the same as in the experiment described above with 50 mgrms. V as Na_3VO_4.

1 mgrm. V as Na_3VO_4 was dissolved in 18 cc. water, 2 cc. 10 per cent NaOH solution were added, and the mixture saturated with H_2S: a deep red colour was finally obtained which was almost the same as that obtained when NH_4OH was used. The experiment was repeated with 20 cc. undiluted NaOH solution: the final colour was the same, but the solution remained colourless for a long time while the H_2S was being passed through it. Therefore the formation of the red compound does not depend on the presence of NH_4OH or $NH_4\times$ ion.

*P. 51*a*, N. 2: *Action of Acids on Sulphovanadate.*—0·5 mgrm. V as sodium vanadate was dissolved in 100 cc. containing about 3 grms. NH_4Cl; 5 cc. NH_4OH (0·90) were added, and the mixture saturated with H_2S: the pink solution was filtered, and then acidified in the cold with acetic acid, stirred, and filtered: a small black precipitate containing sulphur was obtained. This was dissolved by boiling with a little HNO_3 (1·20); the solutions were evaporated to about 2 cc. and 1 to 2 cc. 3 per cent H_2O_2 were added: an orange-yellow colour resulted, showing the presence of a small amount of vanadium. The experiment was repeated with sodium hypovanadate: the results were the same.

The experiment was repeated with 25 mgrms. V: on boiling the filtrate from the precipitate of vanadium sulphide it became blue and sulphur separated. To it 50 mgrms. Fe as $FeCl_3$ were added, and then an excess of NH_4OH: the mixture was filtered, the filtrate was evaporated to dryness, the residue ignited and dissolved in a very little HNO_3, and a few drops H_2O_2 solution were added: no colour appeared, showing that the vanadium in excess of 0·1 mgrm. had been carried down with the $Fe(OH)_3$. The sulphide and hydroxide precipitates were dissolved separately in HNO_3, H_2O_2 was added together with 20 to 30 cc. water, and the intensities of the colours compared: it was estimated that about 10 mgrms. V were precipitated as sulphide, and the remaining 15 mgrms. V with the $Fe(OH)_3$. The experiment was repeated with 50 mgrms. V, a larger amount of $FeCl_3$ being used: the results were similar, thus showing that under these conditions less than half the vanadium is precipitated as sulphide. In other experiments in which the volume was only 20 to 30 cc., and the relative proportion of ammonium salt to NH_4OH was smaller, 80 to 90 per cent of the vanadium was found to be precipitated as sulphide by acetic acid. Even when NaOH was used instead of NH_4OH, it was not possible to precipitate the sulphide completely.

The experiment with 50 mgrms. V described in the last paragraph was repeated, except that HCl was used to

* From the *Journal of the American Chemical Society*, xxx., No. 4.

acidify the cold solution: it was estimated that roughly one-half of the vanadium was precipitated as sulphide and the other half with the $Fe(OH)_3$. The last experiment was repeated, except that the mixture containing HCl was boiled for about one minute: somewhat less than half the vanadium was found in the HCl precipitate.

*P. 51*a*, N. 3: *Complete Precipitation of Vanadium by Ammonium Hydroxide in the presence of Iron.*—See preceding section, and C. E., G. D., Section 1.

*P. 51*a*, N. 4: *Pervanadic Acid.*—See Scheur (*Zeit. Anorg. Chem.*, 1898, xvi., 284); Pissarjewsky (*Zeit. Phys. Chem.*, 1903, xliii., 171 and 173; and 1902, xl., 368).

Action of H_2O_2 *on Vanadic Acid.*—In a series of six test-tubes, each of which contained 1 mgrm. V as Na_3VO_4, were placed 0, 0·5, 2, 5, 10, and 20 cc. H_2SO_4 (1·20); each solution was diluted to 20 cc. and 2 cc. 3 per cent H_2O_2 added: no change was observed in the tube with no acid: the solution became orange to orange-red in the remaining tubes, and the intensity of the colour increased greatly as the concentration of the acid increased. The experiments were repeated with HNO_3 (1·20): the results were the same. All the tubes were allowed to stand over night: no changes in the colours were observed. Ether was added to a number of the solutions and the mixtures shaken: the ether layer remained colourless.

To solutions containing 1 mgrm. V as Na_3VO_4 dissolved in 1 cc. HNO_3 (1·20) were added, (*a*) 1 cc. 3 per cent H_2O_2 and 8 cc. water, (*b*) 3 cc. H_2O_2 and 6 cc. water, and (*c*) 9 cc. H_2O_2: the first two solutions were orange-red, but the third solution was practically colourless, thus showing that a large excess of H_2O_2 spoils the test. To the third solution were added 3 cc. HNO_3 (1·20): the orange-red colour reappeared, thus proving again that the test is more easily obtained in the presence of a large excess of acid. To this solution was then added 7 cc. H_2O_2: the colour became much fainter.

The first series of experiments with varying amounts of HNO_3 (1·20) and a total volume of 20 cc. was repeated, except that 0·1 mgrm. V as Na_3VO_4 was used instead of 1 mgrm.: all the solutions remained colourless, showing that 0·1 mgrm. V cannot be detected in 20 cc. This series of experiments was repeated with 0·3 mgrm. V: a distinct yellow colour could be seen on looking down the tubes in the experiments with 5, 10, and 20 cc. HNO_3, a light colour with 2 cc. HNO_3, and none with 0·5 cc. This series was repeated with 0·5 mgrm. V: with 0·5 cc. HNO_3 the solution was colourless, with 2 cc. it was slightly yellow, and in the remaining experiments a slight but distinct orange-yellow colour was observed. Therefore the limit of detectability of vanadium with H_2O_2 in HNO_3 solution is about 0·5 mgrm. V in 20 cc., and the solution must contain at least 1 volume HNO_3 (1·20) to 3 volumes of water.

*P. 51*a*, N. 5: *Tungstic Acid dissolves in Acids when Phosphate or Arsenate is present.—Tech. Quart.*, 1903, xvi., 122.

Partial Precipitation of Tungsten on Acidifying a Solution of Sulphotungstate.—See *Tech. Quart.*, 1904, xvii., 253—5.

Action of H_2S *on Tungstate dissolved in excess of* NH_4OH.—50 mgrms. W as $(NH_4)_2WO_4$ and 3 grms. NH_4Cl were dissolved in 100 cc. water, 5 cc. NH_4OH (0·90) were added, and the mixture was saturated with H_2S: the solutions remained nearly colourless for over ten minutes, but finally became slightly yellow, probably owing to the formation of polysulphide.

Action of H_2O_2 *on Tungstic and Molybdic Acids* (see *Tech. Quart.*, 1904, xvii., 251). — 20 mgrms. Mo as $(NH_4)_2MoO_4$ were dissolved in 5 cc. HNO_3 (1·20) and 2 cc. H_2O_2 added: a lemon-yellow colour resulted. On account of the absence of an orange tint there is no difficulty in distinguishing between this colour and that of pervanadic acid.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

THE following are abstracts of papers received during the vacation, and published or passed for publication in the *Transactions*:—

164. "*The Use of the Micro-balance for the Determination of Electro-chemical Equivalents and for the Measurement of Densities of Solids.*" By OTTO BRILL and CLARE DE BRERETON EVANS. (*Trans.*, 1908, 1442; this paper was taken as read at the meeting of May 21st, 1908).

By the use of the micro-balance the electro-chemical equivalent of copper is found to be 31·95, and that of antimony 40·9, the amount of metal used being from one-third to one-half of a mgrm. The instrument may also be employed for determining the densities of solids which can be obtained in regular form, and thus measurable with a microscope. Results agreeing with those recorded by previous investigators were obtained by using about half a mgrm. of the substances selected.

165. "*The Preparation of Disulphides.* Part III. *The Nitrobenzyl Disulphides.*" By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS. (*Trans.*, 1908, 1401).

The authors have prepared o-, m-, and p-*nitrobenzyl disulphides* by the action of alkali on solutions of the corresponding nitrobenzyl thiosulphates (compare Price and Twiss, *Trans.*, 1908, xciii., 1395). The solution of the complex thiosulphate is obtained in each case by boiling together an aqueous solution of sodium thiosulphate and an alcoholic solution of the nitrobenzyl chloride. The most satisfactory alkali for the subsequent action is sodium carbonate. The *o*-, *m*-, and *p*-disulphides obtained melt at 109·5°, 103°, and 126·5° respectively.

166. "*The Relation between Unsaturation and Optical Activity.* Part III. *Optically Active Salts of Acids containing Adjacent Unsaturated Groups.*" By THOMAS PERCY HILDITCH. (*Trans.*, 1908, 1388).

The *brucine* and *cinchonine* salts of anthranilic and salicylic acids, and of the acetyl and benzoyl derivatives of these acids, have been prepared and measured polarimetrically, and it is found that, in general, as the number of contiguous unsaturated groups increases, the effect on the optical rotatory power of the alkaloids also increases. Further evidence has been obtained as to the effect on the optical activity of a compound when two unsaturated groups are situated at varying degrees of proximity to each other in the molecule.

167. "*The Constitution of Glucose Derivatives.* Part I. *Glucose-anilide, -oxime, and -hydrazone.*" By JAMES COLQUHOUN IRVINE and ROBERT GILMOUR. (*Trans.*, 1908, 1429).

The behaviour of some glucose derivatives on methylation has been studied with a view to distinguishing between compounds produced from the aldehydic form of the sugar and those derived from the γ-oxidic isomerides. Glucoseanilide, when fully alkylated by the silver oxide reaction, is converted into tetramethyl glucoseanilide (m. p. 132—134°), identical in every respect with the compound previously obtained by condensing tetramethyl glucose with aniline. This result shows that glucoseanilide only contains four hydroxyl groups capable of methylation, and that the compound possesses the γ-oxidic linking characteristic of reducing sugars and glucosides. The compound should thus exist in two stereoisomeric forms (α- and β-), and evidence has been obtained that this is the case. When prepared by condensing glucose and aniline at +6°, a dextrorotatory variety is formed, which, in solution, is converted into the lævorotatory α-isomeride (α_D 20 − 52·3°), thus giving rise to extensive mutarotation. The same phenomenon has also been observed in the case of tetramethyl glucoseanilide in methyl-alcoholic solution.

Glucoseoxime behaves similarly towards the alkylating

mixture of silver oxide and methyl iodide, as pentamethyl glucoseoxime was obtained as the product of maximum methoxyl content. This compound is tetramethyl glucoseoxime methyl ether, as by hydrolysis tetramethyl glucose is produced. From this result it is deduced that glucoseoxime, in addition to reacting as a normal oxime, is equally capable of behaving as a γ-oxide.

Similar methods when applied to glucosephenylhydrazone led to no definite result, owing to extensive oxidation taking place.

168. "*The* cis-*and* trans-*Modifications of* 1-*Methyl*cyclo*hexan*-2-*ol*-4-*carboxylic Acid and their Conversion into* 1-*Methyl*-Δ^1-cyclo*hexene*-4-*carboxylic Acid*." By Andrew Norman Meldrum and William Henry Perkin, Jun. (*Trans.*, 1908, 1416).

The authors have reduced 2-hydroxy-*p*-toluic acid by sodium and alcohol, and find that the product of reduction is readily converted into 1-*methyl*-Δ^1-cyclo*hexene*-4-*carboxylic acid*, $CMe\leqslant\begin{matrix}CH—CH_2\\CH_2\cdot CH_2\end{matrix}>CH.CO_2H$, by treatment first with hydrobromic acid and then with diethylaniline.

169. "*Studies on the Viscosity and Conductivities of some Aqueous Solutions.* Part I. *Solutions of Sucrose, Hydrogen Chloride, and Lithium Chloride.*" By W. Heber Green.

The viscosity of sucrose solutions at 18° and 25°, the viscosity and conductivity of hydrochloric acid at 25°, and of lithium chloride solutions at 18° and 25°, have been measured over ranges of concentration limited only by the solubilities of each substance.

The densities of lithium chloride solutions have been re-determined and compared with the results obtained by previous observers.

The viscosity results obtained show that various formulæ which have been suggested do not at all accurately represent the connection between viscosity and concentration, especially when concentrated solutions are examined. The most concordant result was obtained by using an expression of the form $\eta/\eta_0 = Av/w$, where v = volume of solute, and w = volume of solvent, present per unit-volume of solution.

170. "*Studies on the Viscosity and Conductivity of some Aqueous Solutions.* Part II. *Mixtures of Solutions of Sucrose and Lithium Chloride: a Contribution towards the Elucidation of the connection between Ionic Mobility and the Fluidity of the Solution.*" By W. Heber Green.

The conductivity and viscosity of aqueous solutions have been measured at 25° of three series of mixtures of lithium chloride and sucrose, in which the ratio of the number of lithium chloride molecules to the number of sucrose molecules was 1 : 0·2, 1 : 2·0, and 1 : 20 respectively.

By extrapolation from the results for these mixtures the conductivity and viscosity values have been calculated for a series in which the above ratio was 1 : ∞. In this way the variations in the ionic mobilities at infinite dilution of the salt, concomitant with change of fluidity due to the presence of sugar in solution, were rendered free from some, is not all, disturbing factors.

The curves obtained show that the ionic mobility is not simply proportional to the physical fluidity of the solution, but more nearly to the two-thirds power in the case of lithium chloride and sucrose; with other ions, and other molecules giving rise to viscosity, the exact function varies, and presumably depends on the relative molecular sizes.

With reference to Hartley, Thomas, and Applebey's use of pyridine as an agent for producing viscosity, the author maintains that Stokes's theorem does not hold for a body of molecular size migrating through a medium composed of bodies comparable in size to itself, and, further, that there is no direct evidence for the presence of an aqueous envelope permanently attached to each ion.

No trustworthy method has as yet been established whereby the true ionisation coefficients of a salt can be determined except in solutions of extreme dilution.

171. "*The Reduction of Refractory Oxides by Carbon.*" By Harold Cecil Greenwood. (*Trans.*, 1908, 1483).

A method has been devised for measuring with an accuracy of about $\pm$ 10° the temperatures of reduction of oxides by carbon, the apparatus being suitable for use up to at least 2000°. The reduction temperatures of the oxides of chromium, manganese, uranium, silicon, tungsten, zirconium, and thorium have been measured, and are all found to be far below those previously estimated.

Commencement of the reaction occurs sharply, but the progress of the reduction depends greatly on the intimacy of admixture. The nature of the carbon employed, as also the physical condition of the oxide, exerts a marked influence on the temperature of reduction.

The reactions, so far as the oxides mentioned above are concerned, are found to occur directly between the carbon and the oxide, and are not due to thermal dissociation.

172. "*The Production of Ferro-alloys.*" By Harold Cecil Greenwood. (*Trans.*, 1908, 1496).

This investigation is an extension of the work described in the preceding paper. In the case of some of the oxides studied, for example, silica and manganous oxide, it is found that a "catalytic" facilitation of the reduction takes place when metals such as iron, manganese, and copper are present. This confirms observations made in the technical preparation of ferro-alloys under conditions which are unsuitable for the isolation of the pure metal. The lowering of the reduction temperature appears to be due to mutual chemical affinity of the two metals, and also in some cases to the alloy being more fusible than the refractory metal; no evidence is forthcoming to show that reduction is assisted by the heat of reaction of ferric oxide and carbon when this oxide is added instead of metallic iron.

173. "*The Rapid Electro-analytical Deposition and Separation of Metals.* Part II. *Antimony and Tin. The Employment of a Diaphragm.*" By Henry Julius Salomon Sand. (*Trans.*, 1908, 1572).

By means of the apparatus already described, antimony has been estimated in sulphuric acid solutions and suspensions in the presence of hydrazine sulphate, and also in solutions containing chlorides. A high temperature is maintained, and the potential of the cathode is kept under control.

Tin has been deposited from stannic solutions containing a small amount of free sulphuric acid and a sufficiency of oxalic acid at a temperature near the boiling-point.

Antimony has been separated from tin. Any *b*-stannic acid which may be present must first be converted into the *a*-form. The electrolyte consists of equal volumes of sulphuric acid and water; a small amount of hydrazine sulphate is added, and the temperature maintained at a little above 100°. The maximum auxiliary voltage is 0·65.

The tin is determined electrolytically in the remaining liquid after neutralisation with ammonia and the addition of oxalic acid. After the greater part of the metal has been deposited, it is necessary to add hydrochloric acid and hydroxylamine hydrochloride in order that the electrolyte may be exhausted; a high temperature is maintained. A considerable number of analyses have been carried out in which the combined metals, taken in varying ratios, weighed approximately 1 grm. The time for the deposition of the antimony was usually about twenty minutes, and that for the tin about eighty minutes.

An apparatus which allows the employment of a diaphragm in rapid electro-analysis has been constructed, and tested in the determination of copper and its separation from iron.

174. "*The Measurement of a Homogeneous Chemical change in a Gas.* (*The Thermal Decomposition of Ozone*)." By Herbert Edmund Clarke and David Leonard Chapman. (*Trans.*, 1908, 1638).

It has been commonly supposed that slow pyrogenic changes in gases have their seat principally, if not entirely,

on the walls of the enclosing vessel. The authors have succeeded in demonstrating that this conclusion is not true in the case of the decomposition of ozone. In vessels of German glass, of which the ratio of surface to volume is not too large, the rate of decomposition of ozone at 100° is independent of the area of the surface of the globe, a fact which proves that the change is a homogeneous one.

175. "*The Proteins of Egg-yolk.*" By Robert Henry Aders Plimmer. (*Trans.*, 1908, 1500).

In addition to the protein, vitellin, which contains 1 per cent of phosphorus, and which is insoluble in water, egg-yolk contains a second protein, which contains 0·1 per cent of phosphorus, and which is soluble in water and coagulable by heat.

It can be prepared either by extracting the yolks, after treatment with ether, with a large volume of water, and heating to boiling in the presence of a small quantity of acetic acid, or by boiling the water used for precipitating the vitellin; this is obtained by dissolving the yolk in 10 per cent sodium chloride solution, extracting with ether, and precipitating with 20 volumes of water. The second method gives a purer preparation of this protein.

This protein differs from ovalbumin in its content of nitrogen as also in the amounts of the various nitrogen constituents contained in it when determined by Hausmann's method, so that it is not identical with this protein; its behaviour towards ether also indicates this. The various amounts in which the nitrogen constituents are present in the protein are very similar to those in vitellin, and suggests a close relationship between these proteins in egg-yolk; hence the name of *livetin* is suggested for this new protein.

176. "*The Conductivities of the α-Oximino-fatty Acids.*" By John Kenneth Harold Inglis and Lottie Emily Knight. (*Trans.*, 1908, 1595).

The authors have prepared specimens of the first four of these acids by the action of nitrosulphonic acid on aceto-acetic ester and its derivatives. The conductivities agree fairly closely with those measured by Hantzsch and Miolati. Measurements of the conductivities of the sodium salts and comparison of the acids with one another have indicated that the acids are not all of the same configuration, but that oximinopropionic acid is different from the others. The authors have also found evidence of the existence of two forms of α-oximino-butyric and -valeric acids.

177. "*Studies of the Perhalogen Salts.*" (Part II.). By Charles Kenneth Tinkler. (*Trans.*, 1908, 1611).

The formation of periodides has been further investigated by means of the ultra-violet absorption spectra of solutions of iodine containing a halogen salt. The iodine additive compounds of trimethylsulphine iodide, bromide, and chloride, which may be either (I.) $(CH_3)_3\overset{(IV.)}{S}X{\cdot}I_2$ or (II.) $(CH_3)_3\overset{(VI.)}{S}\begin{matrix}X\\ \diagup\\ -I\\ \diagdown\\ I\end{matrix}$ (X = I, Br, or Cl), gave spectra which are identical with those of solutions of iodine containing potassium iodide, bromide, and chloride respectively. This agreement shows that these substances contain the true perhalogen groups, and affords evidence in favour of Formula I.

The formation of perbromides (by the addition of a bromide to bromine water) has also been investigated by the spectroscopic method, and evidence obtained of the existence of these substances in a large number of cases. Evidence was also obtained of the formation of bromine additive compounds of chlorides.

178. "*The Formation of Ethers from Compounds of the Benzoin Type.*" By James Colquhoun Irvine and David McNicoll. (*Trans.*, 1908, 1601).

The authors find that the methyl ethers of benzoin should always be prepared by the silver oxide reaction, as by the use of Fischer's process of methylation the yields obtained are poorer, and in some instances furan derivatives are formed in quantity. In the case of anisoin, no methyl ether is produced in the latter reaction, which gives rise to the *tetramethoxyl* derivatives of α-methoxy-αβ-dibenzoyldibenzyl (m. p. 218—219°) and of 2-hydroxy-3 : 5-dimethoxytetraphenyltetrahydrofuran (m. p. 263—265°).

The hydrochloric acid method can also be applied to *o*-dimethoxybenzoin only within a limited range of concentration of the acid, as the benzoin readily undergoes molecular rupture to give *o*-methoxybenzoic acid. When the same process is applied to furoin, no methylation takes place, condensation products containing five furyl residues and analogous to those obtained from ordinary benzoin being produced. On the other hand, ethyl ethers of benzoins are comparatively readily prepared by Fischer's method, and no furan derivatives are formed.

In the course of the work, several benzoin ethers have been prepared by the silver oxide method, and the compound described by Limpricht and Jena as "ethyl benzoin" has been examined, and shown to be a mixture of hydrobenzoin and *iso*hydrobenzoin.

179. "*Aromatic α-Disulphones.*" By Thomas Percy Hilditch. (*Trans.*, 1908, 1520).

Aromatic α-disulphones, previously obtained only by the interaction of an aromatic sulphonyl chloride and the sodium salt of an aromatic sulphinic acid, have been prepared in yields varying from 17 to 40 per cent by the oxidation of sulphinic acids by potassium permanganate in glacial acetic acid solution. *Diphenyl*, *di*-p-*phenetyl*, *di*-p-*tolyl*, and *di*-p-*xylyl α-disulphones* have been thus obtained as well-crystallised stable substances of high melting-point; they are decomposed slowly by strong ammonia into a mixture of sulphonamide and sulphinate, and by warm aqueous potassium hydroxide into the corresponding sulphonates and sulphinates.

180. "*The Action of Bromine on β-Hydrindone.*" By Norman Allen Creeth and Jocelyn Field Thorpe. (*Trans.*, 1908, 1507).

The bromination of β-hydrindone may be effected by the action of bromine in chloroform solution, all four hydrogen atoms of the hydrindene ring being replaced by the halogen. A *monobromo*- and a *dibromo*-derivative may also be prepared by using the calculated quantity of bromine, but *ααγ*-tribromo-β-hydrindone cannot be produced in this way, since, when the amount of bromine required for its formation is employed, an equimolecular mixture of αγ-dibromo-β-hydrindone and *ααγγ-tetrabromo-β-hydrindone* is alone formed. The monobromo- and dibromo-derivatives are neutral substances insoluble in alkalis, showing, therefore, that the combination of the halogen with the α-carbon atom of β-hydrindone does not transform the compound into a derivative of hydroxyindene. The action of alkalis on the various bromo derivatives has been investigated, but only in the case of *ααγγ*-tetrabromo-β-hydrindone has a well-defined product been obtained. In this instance, through a curious fission of the hydrindene ring, the product consists of phthalidecarboxylic acid.

181. "*On Polymorphism, with especial reference to Sodium Nitrate and Calcium Carbonate.*" By William Barlow and William Jackson Pope. (*Trans.*, 1908, 1528).

In continuation of their previous work, the authors discuss the relation between the crystalline form and the chemical constitution exhibited in connection with a number of well known cases of polymorphism.

182. "*The Oxidation of Phosphorous Acid by Iodine.*" By Bertram Dillon Steele.

In continuation of the investigation of the reaction between iodine and hypophosphorous acid, the velocity of interaction of iodine and phosphorous acid has been studied. It has been found that two reactions of essentially

different character occur between these reagents, one of which preponderates in more strongly acid solution, and the other, in the presence of feeble acids, such as acetic and boric acids.

The former of these reactions is catalytically accelerated by the presence of hydrogen ions, and the velocity is proportional to the concentration of phosphorous acid (or of the phosphorous ion) and to the square root of the concentration of the iodine.

The conclusion is drawn that reaction takes place between phosphorous acid molecules (or ions) and iodine atoms, the latter being supplied in extremely small but sufficient quantity by the dissociation of the iodine molecules. A slight apparent retardation of the reaction velocity by the iodine is probably due to the incompleteness of the hypothesis which has been suggested to explain the experimental results.

The second reaction, which occurs in the presence of salts, such as sodium acetate, bicarbonate, or biborate, is so complex that the attempt to formulate a hypothesis explanatory of the reaction has been abandoned. The reaction is accelerated by the presence of phosphorous acid, and of sodium acetate, and retarded by the presence of iodine and of potassium iodide.

183. "*The Direct Interaction of Magnesium and Alkyl Halides.*" By JAMES FREDERICK SPENCER and MARY S. CREWDSON.

It has been found that all alkyl halides react directly with magnesium. The halides of hydrocarbons lower in the series than butane only react when heated in a sealed tube, but, with the exception of the chlorides, which, so far as has been investigated, appear always to require heating in a sealed tube, all the halides of hydrocarbons higher in the series than butane react with magnesium when the two substances are heated together in a flask. The products are magnesium alkyl halides and hydrocarbons containing twice as many carbon atoms as the original halide. In the reactions taking place in sealed tubes, unsaturated hydrocarbons, of both the acetylene and the olefine series, together with much hydrogen, are also found, in addition to the above-mentioned compounds. Methyl bromoacetate also reacts directly with magnesium, giving good yields of methyl acetate and dimethyl succinate, and aromatic chloro-derivatives react with magnesium when heated with it in a sealed tube, yielding the corresponding hydrocarbons in good yield.

(To be continued).

THE ROYAL SOCIETY.

THE following is a list of the Fellows recommended by the President and Council of the Royal Society for election into the Council for the year 1908-9 :—

President.—Sir Archibald Geikie, K.C.B., D.C.L., Sc.D., LL.D.

Treasurer.—Alfred Bray Kempe, M.A., D.C.L.

Secretaries.—Professor Joseph Larmor, D.Sc., D.C.L., LL.D., and Professor John Rose Bradford, M.D., D.Sc.

Foreign Secretary.—Sir William Crookes, D.Sc.

Other Members of Council.—Sir George Howard Darwin, K.C.B., Professor James Cossar Ewart, M.D., Sir David Gill, K.C.B., John Scott Haldane, M.D., Charles Thomas Heycock, M.A., Professor Horace Lamb, D.Sc., Professor Hector Munro Macdonald, M.A., Frederick Walker Mott, M.D., the Hon. Charles Algernon Parsons, C.B., Professor William Henry Perkin, Ph.D., Professor Edward Bagnall Poulton, D.Sc., Lieutenant-Colonel David Prain, C.I.E., Sir Arthur William Rücker, D.Sc., the Right Hon. Sir James Stirling, LL.D., Professor Frederick Thomas Trouton, Sc.D., and Willlam Whitaker, B.A.

NOTICES OF BOOKS.

Laboratory Arts. By GEORGE H. WOOLLATT, Ph.D., F.I.C. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1908.

THE author of this book has had special opportunities, during the summer courses for science teachers held in Ireland and Yorkshire, of finding out at first hand what problems in the construction and repair of all kinds of apparatus are most generally met with in laboratories, and he has turned his opportunities to the best account in the preparation of the book. It describes the use of tools for wood, metal, and glass work, and gives directions for the construction of various pieces of apparatus, some of them fairly complicated. Indeed, in some cases, more especially in glass work, it would seem that the cost of the finished article was out of proportion to the time and trouble which would have to be expended in its preparation in the laboratory. The sections on wood and metal work contain many suggestions which might be adopted in manual training classes, for which simple apparatus provides interesting and not unduly difficult exercises. In large laboratories at any rate, the value of the general information relating to the care of bench tops, the labelling of bottles, electrotyping, &c., which is given in the fourth section, would very soon repay the cost of the book.

Post's Chemisch-Technische Analyse. ("Post's Chemical Technical Analysis"). Edited by Prof. BERNHARD NEUMANN. Vol. II., Part III. Braunschweig: Friedrich Vieweg und Sohn. 1908.

THE third part of the second volume of this text-book contains comprehensive accounts of practical methods of analysing fertilisers, ethereal oils, tobacco, rubber, explosives, tanning materials, and some other substances. Each chapter has been prepared by an expert who has a thorough knowledge of the subject entrusted to him, and only the most modern and trustworthy methods find a place in the book. Both as a work of reference and as a laboratory guide "Post's Chemisch-Technishe Analyse" has every good feature to recommend it, and no scientific library should be regarded as complete unless it includes a copy of the third edition.

CORRESPONDENCE.

THE WAVE THEORY OF MOTION.

To the Editor of the Chemical News.

SIR,—I have read Mr. John McDowall's paper on the above subject in the CHEMICAL NEWS of October 30 (vol. xcviii., p. 213) with very great interest. By a line of reasoning different to that employed by him, I had already concluded that, granting the objective reality of time and space, it was not improbable that time is the "fourth dimension," and that the whole of the physical universe is moving in this timal direction.

On Friday, April 3, 1908, I had the honour of reading to the Polytechnic Mathematical Society a paper in which this view was expressed. In this paper I enunciated what I believe to be a new mathematical proof of the real existence of not only a fourth but an infinity of dimensions, providing that space itself is real. This proof will be found very briefly stated in a letter to the editors of *Knowledge and Scientific News* (vol. v., p 157, July, 1908). In the paper above mentioned I also applied this proof to time, and pointed out that time possessed the properties expected of a fourth dimension. This view, namely, that time is the "fourth dimension," is, however, not an original one, but it has generally been accompanied by the assumption that matter

is itself four-dimensional and extends through time, and that it is our consciousness that travels in a timal direction. In the above mentioned paper I rejected this hypothesis and suggested as more likely that the whole physical universe is rushing through time, as this would, at least so it appears, explain why time appears to us to be so different from length in space, and also why we have no consciousness of higher dimensions. I did not, however, mention these speculations in the letter to the editors of *Knowledge and Scientific News*, but about a month or two ago I prepared a revised essay on the subject which has since been pending publication.

In conclusion, I am most happy that Mr. McDowall's line of reasoning regarding the nature of motion should have confirmed my speculations regarding the fourth dimension, and I would be glad, if he should care to read it, to forward Mr. McDowall a copy of my original paper, in which this particular view is, I believe, first expressed, as the publication of the revised paper may be delayed for some time.—I am, &c.,

H. Stanley Redgrove.

The Polytechnic, Regent Street, W.,
October 30, 1908.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xli., No. 13, 1908.

Decomposition of Chromic Acid by Hydrogen Peroxide.—E. H. Riesenfeld.—The reaction between hydrogen peroxide, potassium bichromate, and sulphuric acid occurs according to the equation—

$$K_2Cr_2O_7 + 7H_2O_2 + 4H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + 11H_2O + 5O_2,$$

when excess of hydrogen peroxide is present. The concentration of the sulphuric acid does not affect the reaction until the strength is 2·5 N, when some Caro's acid is formed, and gives up oxygen much quicker than hydrogen peroxide. When excess of chromic acid is present the equation is—

$$K_2Cr_2O_7 + 3H_2O_2 + 4H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O + 3O_2,$$

and again the reaction is independent of the concentration of the sulphuric acid until the strength of the latter has been increased above 2·5 N. These two reactions of hydrogen peroxide with Cr_2O_7 may be represented by the ionic equations. I. In presence of excess of hydrogen peroxide,

$$Cr_2O_7'' + 7H_2O_2 = 2CrO8''' + 4H^{\cdot} + 5H_2O,$$
$$2CrO8''' + 12H^{\cdot} = 2Cr^{\cdots} + 6H_2O + 5O_2.$$

II. In presence of excess of chromic acid,—

$$Cr_2O_7'' + 3H_2O_2 = 2CrO_5' + 3H_2O,$$
$$2CrO_5' + 8H^{\cdot} = 2Cr^{\cdots} + 4H_2O + 3O_2.$$

The author's researches show that chromic acid and chromates are never reduced by hydrogen peroxide directly to chromic oxide salt, but that perchromates are always formed, and these in acid solution give up oxygen and form chromic salts.

Preparation and Constitution of Sulphoxides and Disulphoxides.—O. Hinsberg.—Sulphides are converted into sulphoxides and disulphides into disulphoxides by the action of hydrogen peroxide in the cold. The formula of disulphoxide might be R.SO.SO.R or R.S.SO_2R. Since, however, the divalent sulphur of the sulphide is oxidised by hydrogen peroxide at any rate at room temperature to the SO group only, for sulphoxides and not sulphones are formed, the disulphides are in all probability converted into oxidation products of formula R.SO.SO.R, tetravalent sulphur being formed. The chemistry of sulphur gives us no reason for thinking that the group .SO.SO. is labile, but rather that it is stable, and hence the disulphoxides have in all probability the formula R.SO.SO.R. When disulphoxides are boiled in alcoholic solution with alkali large quantities of disulphides are formed. This reaction is very easily explained if it is assumed that alkalis transform the disulphoxides into unstable thioesters, which then yield disulphides, R.SO.SO.R $\rightarrow$ R.S.SO_2.R $\rightarrow$ R.S.S.R.

Sodium Compound of Fluorene.—R. Weissgerber.—When sodamide is introduced into fluorene heated to 120°, ammonia is evolved, and sodium fluorene separates out as a brownish yellow mass. When the mixture is heated to about 150° and allowed to cool, a brownish yellow crystalline mass is formed. The compound has the formula $C_6H_4 \gtrless CH.Na$. The preparation of this substance can conveniently be used to separate fluorene from coal-tar mixtures on a large scale. None of the hydrocarbons which accompany fluorene in coal-tar, acenaphthene, phenanthrene, &c., form a sodium compound. The fluorene-sodium can be separated by mechanical means from the mixture, and the fluorene recovered by decomposing it with water, distilling off the raw fluorene, and allowing it to crystallise.

Ultra-violet Fluorescence in Cyclic Compounds.—H. Ley and K. von Engelhardt.—The authors have investigated the mono- and di-substitution products of benzene with reference to their ultra-violet fluorescence, using Stark's method. Alcoholic solutions of concentration 0·005 normal were employed. The most important results obtained were as follows :—*Hydrocarbons.*—Toluene and propyl benzene have a much stronger fluorescence than benzene. The four bands characteristic of benzene disappear. *Amino Compounds.*—Aniline shows a much stronger fluorescence than benzene, also β-naphthylamine fluoresces more strongly than aniline. Dimethylaniline shows distinct fluorescence, which, however, is less than that of aniline. *Hydroxyl Compounds.*—The hydroxyl and methoxyl groups increase fluorescence; thus phenol and anisol exhibit the phenomenon very strongly. Benzoic acid fluoresces feebly, oxybenzoic acid more strongly; of the isomeric oxybenzoic acids the ortho-compound shows the strongest fluorescence and the para-compound the weakest. *Halogen Compounds.*—The halogens act like the carboxyl group, and their action is more marked the higher the molecular weight is. *Benzonitrile and Benzamide.*—Benzonitrile fluoresces strongly, while benzamide does not exhibit the phenomenon. *Nitro Compounds.*—The nitro group usually hinders fluorescence.

Picrates.—O. Anselmino.—When picric acid or yellow ammonium picrate is heated in 10 per cent ammonia solution to 80°, blood-red crystals are formed containing one molecule of acid to one molecule of ammonia. When these red crystals are re-crystallised they yield only the usual light yellow needles of ammonium picrate. The author has not yet decided whether the red colour of the first crystals is due to an impurity which has arisen from the action of hot alkali on picric acid.

Iodopentamminocobaltic Salts.—A. Werner.—The compounds obtained by J. Sand and G. Böckmann by the action of iodine on black nitrosopentamminocobaltic salts belong to the hitherto unknown iodopentamminobaltic series, and have the general formula $\left[Co^{I}_{(NH_3)_5}\right]X_2$. Aquopentamminocobaltic iodide, $\left[Co^{OH_2}_{(NH_3)_5}\right]I_3$, when heated to 80°, readily loses water, yielding a brown difficultly soluble product which, with ammonium nitrate, gives a good yield of green iodopentammincobaltic nitrate. This shows, beyond doubt, that the salts belong to the

iodopentammin series. The colours of the halogen pentammincobaltic salts are as follows:—

$\left[Co^{Cl}_{(NH_3)_5}\right]X_2$, Purple. $\left[Co^{Br}_{(NH_3)_5}\right]X_2$, Violet-blue. $\left[Co^{I}_{(NH_3)_5}\right]X_2$, Green.

Relations between Nickel and Hydrogen.—M. Mayer and V. Altmayer.—The authors have investigated the absorption of hydrogen by nickel at constant volume, the pressure of the hydrogen and the temperature being altered. The pressure was increased from one-fifteenth to four-fifths of an atmosphere and the temperature from 360° to 560°, and the volume of hydrogen absorbed by the nickel was observed. It was thus found that the graphs obtained were straight lines corresponding to Henry's law; *i.e.*, the masses of gas taken up are directly proportional to the pressure. Thus the system nickel-hydrogen is bivariant.

Methane Syntheses with Calcium Hydride.—M. Mayer and V. Altmayer.—Calcium hydride may be prepared by passing hydrogen over metallic calcium in turnings at a temperature which is gradually raised from 270°. The hydride thus obtained is grey in colour and can easily be powdered. It falls to a powder in air, and is decomposed by water and dilute acids, giving hydrogen. When carbon monoxide is led over the hydride at temperatures from 400° to 800°, methane is formed, and a black residue mixed with a little grey substance is left behind. This residue smells slightly of acetylene. When it is treated with water, gas is energetically evolved, and a strong smell, first of acetylene and then of ammonia, is noticed. The reaction seems to be as follows:—

$$3CaH_2+3CO=CH_4+3CaO+2C+H_2,$$
$$CaH_2+2C=CaC_2+H_2.$$

When carbon dioxide replaces the monoxide in this experiment the reaction is represented by the equation $2CO_2+4CaH_2=CH_4+4CaO+C+2H_2$. The residue resembles the former residue in appearance, but has no smell. When water is added to it no gas is evolved till the mixture is heated, then a slight smell of acetylene is noticed. With dilute hydrochloric acid carbon dioxide is evolved. When carbon acts on calcium hydride some methane is evolved above 270°. The residue is black, and smells of acetylene. It gives large quantities of gas when treated with cold water, and strong smells, first of acetylene and then of ammonia, are observed. The interior of the flask in which the residue is treated with water becomes very hot.

Action of Hydrazine Hydrate on Bisdiazoacetic Ester.—Th. Curtius and Eugen Rimele.—The first product of the action of hydrazine hydrate on bisdiazoacetic ethyl ester is bisdiazoacetic acid ethyl ester hydrazide, $COOC_2H_5.C\overset{N\cdot\!\!-\!\!-\!\!-N}{<NH-NH>}C.CO.NH.NH_2$. The further action of the hydrazine hydrate converts this compound into bisdiazoacetic acid bishydrazide, $NH_2.NH.CO.C\overset{N\cdot\!\!-\!\!-\!\!-N}{<NH-NH>}C.CO.NH.NH_2$. Thus bisdiazoacetic ester reacts with hydrazine hydrate like terephthallic acid ester, which also yields an ester hydrazide. Bisdiazoacetic acid ethyl ester hydrazide is oxidised by nitrous acid to tetrazinedicarboxylic acid ethyl ester azide, $COOC_2H_5.C\overset{N-N}{<N=N>}C.CO.N_3$, and, similarly, the bishydrazide yields a bisazide. The authors have prepared the neutral hydrazine salt of bisdiazoacetic acid and a series of acid salts of bisdiazoacetic acid; they have thus found that only the monovalent alkali metals and the monovalent diammonium group are capable of forming acid salts.

A Zirconium-mercury Double Salt.—Walter Peters.—Dry pure zirconium tetrachloride reacts with mercury phenyl when they are heated together in a tube which is exhausted by means of a water air-pump. The equation is $ZrCl_4+2Hg(C_6H_5)_2+H_2O=ZrOCl_2.2HgClC_6H_5+2C_6H_6$. The double salt thus obtained is exceedingly soluble in ether. The mercury is evidently not bound directly to the zirconium, for when the double salt is heated *in vacuo* mercury phenylchloride sublimes, and thus the salt is undoubtedly a molecular compound.

Salts of an Acetato-chromium Base.—R. F. Weinland.—By warming chromic acid with glacial acetic acid two crystalline compounds can be obtained. One, a brownish black substance, contains seven molecules of acetic acid and two of chromic acid to three atoms of trivalent chromium, and the other, which is dark green, contains seven molecules of acetic acid and one molecule of chromic acid to three atoms of trivalent chromium. They appear to be chromate acetates of a triacidic acetato-chromium base, $\left[Cr_3{}^{(CH_3CO.O)_6}_{H_2O}\right]^{(OH)_8}$, the first being the bichromate-acetate and the second the chromate-acetate of the same base. Two more chromate-acetates, a chloride-chromate, a nitrate-acetate, and a biacetate may be prepared from this base, as well as a platinum chloride salt. The normal salts of the base have a strong acid reaction in aqueous solution, the basic salts with one hydroxyl group, such as the chloride acetate, have a faint acid reaction. A freshly prepared solution of the chloroplatinate, which contains two hydroxyl groups, is at first neutral, but after a time it becomes feebly acid. All salts of the base with colourless acids are green. The free acetato-chromium base may be prepared in aqueous solution by grinding up an excess of silver oxide in a concentrated solution of the chloride acetate, and filtering after a short time. Thus a dark green alkaline liquid is obtained. This gradually loses its alkaline reaction, and becomes, first, neutral, and finally feebly acid. The acetic acid residue migrates from the cation, and the solution on evaporation gives some silver acetate and biacetate. The acetato base is quite stable in acid solution, but gradually decomposes in the free state. An iron base corresponding to this chromium base is contained in a solution of ferric hydroxide in glacial acetic acid. By the addition of chromic acid to such a solution red crystalline bichromatacetate of formula $\left[Fe_3(CH_3CO.O)_6\right]^{Cr_2O_7.H_2O}_{(CH_3CO.O)}$ is obtained. Similar aluminium compounds also appear to exist. By heating chromic acid with glacial acetic acid and concentrated sulphuric acid, a compound is obtained in the form of a very hygroscopic green powder consisting of trivalent chromium, acetic acid, and sulphuric acid.

Action of Cold Caustic Soda Solution on Cellulose.—W. Vieweg.—When cold caustic soda solution acts on cellulose within concentration limits of 11 to 24 per cent, caustic soda is taken up by the cellulose in the proportions corresponding to the formula $C_{12}H_{19}O_{10}.Na$. The curve representing the absorption of NaOH from caustic soda solution by cellulose has a kink at this stage. If the caustic soda solution is saturated with sodium chloride when the concentration is low, this kink appears at a lower concentration the higher the degree of mercerisation and the greater the amount of common salt in the liquid. Before the kink the curve is irregular, which points to a chemical reaction consisting of an increase in the degree of mercerisation. After the kink the curve becomes a horizontal straight line. The addition of sodium chloride to the alkali up to the saturation point leads to a chemical and physical reaction (adsorption) between caustic soda solution and cellulose.

NOTES AND QUERIES.

Blue Ink.—I was recently shown an engraving printed in blue ink on white paper. Half of this engraving had been soaked in some chemical which had changed the blue ink to a bright green, without in any way affecting the white paper on which it was printed. Green printer's ink can easily be changed to blue by soaking it in oxalic acid, but I have as yet been unable to find out how blue can be changed to green. If any reader is able to give me the information I should be greatly obliged.—F. Baker.

THE CHEMICAL NEWS.

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THE PRESENT STATE OF OUR KNOWLEDGE OF RADIO-ACTIVITY.*

By A. DEBIERNE.

Part I.—*The Discovery of the Radio-active Substances.*

At the present time radio-activity comprises a great number of facts and theories; its development has been extremely rapid, and its importance is quite comparable with that of much older sciences, such as physical chemistry. To show the magnitude of the subject I need only mention that a course of radio-activity, lasting the whole year, is held at the Sorbonne, the professor being Mdme. Curie.

H. Becquerel was the first to observe the fundamental phenomena in the compounds of uranium, and the results of his first experiments show at once what is meant by a radio-active substance.

The salts of uranium possess the property of spontaneously emitting a radiation which is capable of acting on a photographic plate, and of making gases conductors of electricity; when a radio-active substance emits a sufficiently intense radiation the radiation may cause the visible phosphorescence of certain substances.

Various chemical actions may give rise to the phenomena of phosphorescence and to conduction by gases. For instance, the oxidation of phosphorus causes the emission of light, and the surrounding gases become conductors of electricity; the same thing happens with sulphate of quinine, when it is subjected to a rapid change of temperature. But in these cases an essential characteristic of radio-active phenomena is lacking; the production of the phenomena is not spontaneous, but it is caused by external actions which may easily be determined.

Mdme. Curie, by her first experiments, gave a rigorous demonstration of another fundamental property of radio-active substances, namely the atomic nature of the property of radio-activity. This spontaneous emission of rays is an essential characteristic of the uranium atom; it is not influenced by the state of combination, and is maintained unaltered in all the compounds of uranium.

This is a very rare phenomenon, and of all the numerous properties of matter, mass is the only one which persists through transformations of a chemical nature, and which also manifests itself spontaneously.

Some time after Becquerel's discovery, Mdme. Curie and Schmidt showed that the compounds of thorium give rise to the same phenomena as the compounds of uranium.

I.

Exact measurements of the intensity of the radiation emitted by radio-active substances are indispensable in all researches in radio-activity; they are generally performed by determining the conductivity of gases which have been exposed to the rays. The photographic action and the phenomena of phosphorescence cannot be used for measurements, but may be very useful for qualitative observations. I will now shortly describe the different forms of apparatus used in measuring radio-activity.

It has been shown that the conductivity of gases is due to the presence of electrically charged particles which are called ions. The rays which cause the conductivity produce positive and negative ions in the gas; these move in an electric field, and deposit their charges on electrified substances.

The current of electricity produced by this movement of the ions may be measured either with a gold-leaf electroscope or else with a quadrant electrometer. The simplest way is to determine the rate of movement of the gold-leaf of the electroscope, or of the needle of the electrometer. In the case of the electroscope the electric field is generally produced between a charged conductor supporting the gold-leaf and a plate upon which the active substance is placed, and which is connected with the case of the instrument. The rate of movement may be measured by observing the gold-leaf with a little microscope provided with a micrometer, and by determining the time taken to move from one fixed division to another.

With an electrometer a specially constructed condenser is generally employed. It consists of two plates; on one of them, which is raised to a high potential, the substance is placed; the other is connected with one pair of the electrometer quadrants. The needle of the electrometer is also raised to a high potential, and the rate of displacement of the luminous spot on a divided scale is determined.

Measurements with the electroscope are very simple to take, and are capable of great sensitiveness; frequent calibrations are necessary, but they may be performed very quickly with a substance of constant activity, such as uranium, aud a great deal of valuable work has been done with this instrument.

Nevertheless, the method which gives the most reliable results is that which was employed by Pierre Curie and Mdme. Curie in their researches, and which is called the quartz piezo-electric method. In this method the phenomenon discovered some time ago by Pierre and J. Curie, and called piezo-electricity, is used. The phenomenon is as follows:—When certain crystals are subjected to mechanical deformations electric charges are produced on certain faces. Thus, when a tensile force is applied to a sheet of quartz cut in a certain manner with regard to the axes, charges of electricity equal in magnitude and of opposite sign are produced on two faces. The quantity of electricity depends upon the dimensions of the sheet, and is exactly proportional to the weight to which the tensile force is due. In the quartz piezo-electric method these charges are used to neutralise the charges brought by the gaseous ions to the plate of a condenser; thus, for example, the time is observed in which the charge developed on the quartz plate by the tension of a given weight is exactly neutralised by the electric charges brought by the ions. In this method the measurements are independent of the arrangement of the apparatus, and the absolute value of the currents can easily be calculated.

II.

Besides the elements uranium and thorium, which are the only ones of the chemical elements previously known to show marked radio-activity, other substances exist with an infinitely greater radio-activity.

The discovery of the most important of these new substances is due to Pierre Curie and Mdme. Curie, who at the same time provided a new method of searching for chemical elements. The rapid development of radio-activity is the outcome of this new method of research and of the discovery of radium.

This last discovery is one of the most remarkable achievements effected in physical science, both as regards the logical development of the researches and the manipulative difficulties which have been overcome. It recalls the discovery of spectral analysis by Kirchhoff and Bunsen, and its immediate result—the isolation of the new alkaline metals, cæsium and rubidium. But the difficulties of demonstrating the existence of radium as a new chemical element and of obtaining its salts in the pure state were much greater.

In the first place, Pierre Curie and Mdme. Curie worked out a method of measurement which enabled the new property to be determined exactly; this was the quartz piezo-electrique method, which is still the most accurate for all researches in radio-activity. Then came the experi-

* *Revue Générale des Sciences*, 1908, xix., 691.

ments of Mdme. Curie, which proved indisputably the atomic nature of the new property, and showed that, of the elements then known, only uranium and thorium are radio-active to an appreciable extent. Then minerals were examined; only those which contain uranium or thorium were found to be appreciably radio-active. But here an important anomaly was observed; the radio-activity of the minerals was sensibly greater than that which would be due to a certain proportion of uranium or of thorium. Hence, in spite of the novelty of the phenomenon, the following conclusion was drawn, viz., that the minerals must contain new chemical elements more strongly radio-active than uranium and thorium. Experiments to separate them were immediately begun.

A small quantity of pitchblende was subjected to chemical treatment by the two physicists, who had no equipment for this kind of work, but hoped that their incursion into the domains of chemistry would be brief, and that they would soon be able to return to the purely physical study of the phenomenon. A first confirmation was soon obtained; substances more radio-active than uranium and thorium can be separated. The existence of new chemical elements in these substances was immediately affirmed; one received the name polonium, the other was called radium. The first hypothetical element is allied to the metals which are precipitated by sulphuretted hydrogen, the second to the metals of the alkaline earths. The results of the separations were always substances which were more and more active, of course in diminishing quantities, and it was soon evident that a larger amount of material would have to be treated. Several kilogrms. were used, and then the rudimentary equipment which was at the disposal of the investigators made the chemical operations very tedious: in spite of this new attempt the same result was obtained; that is to say, substances of increasing activity were prepared, but the activity did not tend towards a limit, and when all the activity had been accumulated in some centigrms. of substance, the latter always appeared to contain a very large proportion of inactive elements. However, during these experiments a confirmation of the existence of one of the new elements gave much encouragement to the investigators to continue their researches. The material containing the hypothetical element radium was examined spectroscopically by Demarçay, who detected a new line, at first very faint, beside those of barium, of which the substance was principally composed; as the activity was concentrated the line became more distinct. The exceeding faintness of the new line showed that the only hope of obtaining pure salt lay in treating several tons of material, and this enormous piece of work was at once begun. The mineral being too expensive, waste products which might contain the new element were obtained from a manufactory; the first treatment was carried out in a factory; the last concentrations, which comprised several hundred fractional crystallisations, were performed in the laboratory, still with the same rudimentary equipment. And after several years of incessant work a sufficient quantity of pure salt (about 1 decigrm.) was obtained. It gave an entirely new spectrum, and the atomic weight of the new element could be determined. According to Mdme. Curie's latest determinations the value is 226·5.

Radium is the only new radio-active substance which has been obtained in a state of purity; it must be mentioned that it is also the only substance the isolation of which has been seriously attempted.

The chief very strongly radio-active substances which have been obtained besides radium and polonium are actinium, which I discovered in pitchblende, radio-thorium, which was discovered by Hahn in thorianite, and ionium, which has quite recently been described by Rutherford and Boltwood. We shall see presently that radio-thorium is closely related to thorium and polonium to radium.

The chemical differences between the various substances are as follows:—Radium, which is the only one that has been obtained as a pure salt, has well characterised chemical properties, which show clearly that it is the last member of the series of the alkaline earths. Its sulphate is still more insoluble in water than barium sulphate; its soluble salts (chloride, bromide, nitrate) are isomorphous with those of barium; the complete separation of the two elements has been effected by fractional crystallisation.

The properties of the metal would be of great interest, but its preparation appears to be as difficult as that of metallic barium, and it has not yet been effected. The operation would involve serious risks of loss of material, and it can readily be understood that the investigators hesitate to undertake it.

In many reactions—precipitation by sulphuretted hydrogen, formation of basic salts—polonium is carried down with bismuth; it may, however, be precipitated by stannous chloride with mercury and tellurium; it may also be partially deposited on plates of silver, bismuth, and even platinum. It has been shown that its activity gradually diminishes.

Actinium has been obtained mixed with the earths which are precipitated by oxalic acid in acid solution, and which do not dissolve in hydrofluoric acid; thus it accompanies thorium and the rare earths. If a fractionation is carried out by the method of the double nitrates of the magnesium series, it passes into the more soluble portions of the ceric earths with neodymium and samarium.

Finally, with regard to radio-thorium but little is known as to its chemical properties; it is only known that it is generally carried down with iron.

As a matter of fact, except in the case of radium, the salts of which have been obtained in a pure state, no definite information can be given regarding the chemical properties of these substances until they have been completely separated from the foreign matter which accompanies them.

In spite of the intense radio-activity which some of them exhibit, they are still in a very diluted state, and the chemical separations which may be observed must be regarded only as the carrying down of them by certain known elements. This has not been understood by some experimenters, who, basing their opinion upon slight chemical differences, have reported the existence of new substances, which have afterwards been recognised as identical with substances already known.

Thus a substance identical with polonium has for some time been called radio-tellurium; another, which is identical with actinium, has received the name emanium. To avoid such confusion we must not rely only upon chemical concentration processes, but the special radio-active properties of each substance must be examined. We shall see that it is very easy to distinguish the different substances from one another, using their radio-active properties only.

(To be continued).

THE

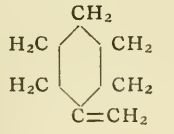
STUDY OF HYDRO-AROMATIC SUBSTANCES.*

(Concluded from p. 228).

Recent Work on Hydro-Aromatic Substances.

Hydrocarbons. — Methylenecyclohexane (I.) has been submitted to detailed investigation by Faworsky and Borgmann (*Ber.*, 1907, xl., 4863), who conclude that the hydrocarbons of this supposed constitution, previously described by Sabatier, Wallach, and Zelinsky and Gutt, are in reality mixtures of methylenecylohexane and 1 : methyl-Δ^1-tetrahydrobenzene (II.). For the preparation of the pure hydrocarbon cyclohexylcarbinol, obtained by the Grignard reaction from bromohexahydrobenzene, was converted into the corresponding iodide, and this latter body heated with alcoholic potash.

* Report of the Committee, consisting of Dr. E. Divers (Chairman), Prof. A. W. Crossley (Secretary), Prof. W. H. Perkin, Dr. M. O. Forster, and Dr. H. R. Le Sueur. Read before the British Association (Section B), Dublin Meeting, 1908.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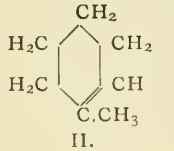
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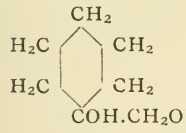
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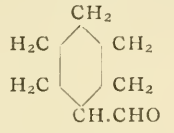
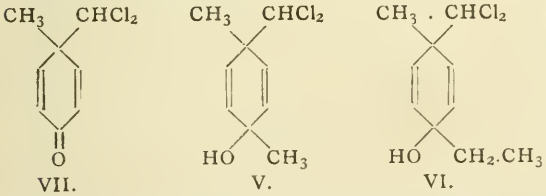

IV.

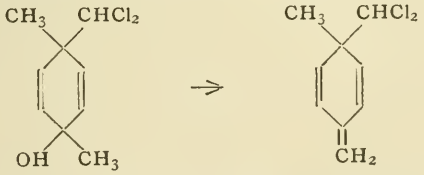
Methylenecyclohexane absorbs two atoms of bromine, and the resulting dibromide gives, on warming with 10 per cent potassium carbonate solution, the glycol having Formula III. When treated with very dilute sulphuric acid this glycol gives an aldehyde (IV.), which can also be obtained directly from the dibromide by treatment with lead oxide and water. These facts conclusively prove the constitution of the dibromide and of the hydrocarbon.

Methylenecyclohexane is unaltered on boiling with quinoline, but is converted by a mixture of quinoline and quinoline-hydriodide into the isomeric methyltetrahydrobenzene (II.). This fact would account for the hydrocarbon obtained by Zelinsky and Gutt from the iodide of cyclohexylcarbinol by heating with quinoline, being a mixture of the two isomerides.

Auwers (*Annalen*, 1907, ccclii., 219, 273, 288) has shown that the alcohols V. and VI., prepared from the ketone VII. by Grignard's reaction, lose water to give unstable intermediate products, which readily pass into benzene derivatives. These reactions—

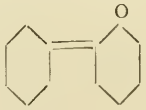

VII. V. VI.

have been very fully investigated, and are described in detail in this lengthy memoir. The hydroaromatic alcohols V. and VI. and their homologues are not very stable substances, and many, if not all, exist in two modifications, probably due to *cis* and *trans*-isomerism. The above-mentioned intermediate products are considered to be alkylidenedihydrobenzenes—



the general chemical and physical properties of which substances are discussed, compared with other closely related compounds, and shown to support the above conclusions as to their constitution.

Ketohexahydrobenzene is acted on by dry hydrogen chloride (Wallach, *Ber.*, 1907, xl., 70) to give a substance having the formula $C_{12}H_{19}OCl$, which loses the elements of hydrogen chloride to give cyclohexene-2-cyclohexanone.



When this dicyclic ketone is reduced it yields the corresponding saturated alcohol, and this, by treatment with hydrogen iodide, the fully hydrogenised dicyclohexyl $C_6H_{11}.C_6H_{11}$.

Alcohols. — Aromatic quinones give (Sabatier and Mailhe, *Comptes Rendus*, 1908, cxlvi., 57), when treated with hydrogen in presence of reduced nickel, a variety of products, the nature of which depends largely on the reaction temperature ; if moderately low the dihydric alcohols of the hexahydrobenzene series are formed.

Monohydric alcohols may be obtained (Hell and Schall, *Ber.*, 1907, xl., 4162) by the action of various alkyl magnesium iodides on ethyl hexahydrobenzoate. The latter is readily prepared by treating cyclohexylmagnesium iodide with carbon dioxide.

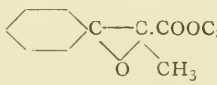
Ketones.—The action of light on ketohexahydrobenzene and the three isomeric ketomethylhexahydrobenzenes has been studied by Ciamician and Silber (*Ber.*, 1908, xli., 1071), who find that the ring is broken with production of a fatty acid containing the same number of carbon atoms together with the corresponding unsaturated aldehyde.

Not only ketohexahydrobenzene itself (*B.A. Reports*, 1907, 110), but also a number of other simple ring ketones, such as ketomethyl- and ketomethylisopropylhexahydrobenzene, are found to be capable of reacting in the enolic form (Mannich and Hänen, *Ber.*, 1908, xli., 564).

The influence of a very reactive agent, for example acetic anhydride, is necessary to bring about the change, and the resulting acetates are converted on saponification into the original ketonss.

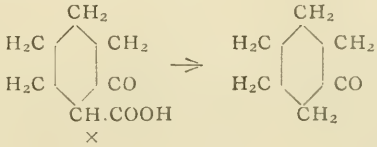
Homologues of ketohexahydrobenzene may be prepared by the slow distillation of the anhydrides of substituted pimelic acids (Blanc, *Comptes Rendus*, 1907, cxliv., 1356).

Ketohexahydrobenzene and the three isomeric ketomethylhexahydrobenzenes condense with ethyl α-chloropropionate (Darzens, *Comptes Rendus*, 1907, cxliv.) in presence of sodium ethoxide, to the corresponding glycidic esters, the product in the first case having the formula—

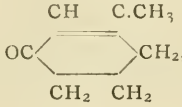


On saponification these esters give free acids, which decompose on distillation in a vacuum, giving hexahydroacetophenone or its homologues. This latter ketone is, however, best prepared (Hell and Schall, *Ber.*, 1907, xl., 4162) by treating the magnesium compound of cyclohexyliodide with acetaldehyde, and oxidising the resulting methylcyclohexylcarbinol $C_6H_{11}.CHOH.CH_3$ with chromic acid.

In the preparation of ketones by elimination of carbon dioxide from ketocarboxylic acids, Kötz (*Annalen*, 1907, ccclvii., 192) finds that the reaction takes place readily in the case of 1-ketohexahydrobenzene-2-carboxylic acid, but it does not proceed at all with acids and less readily with alkalis, as the hydrogen atom marked with a × is replaced by methyl, ethyl, or isopropyl.

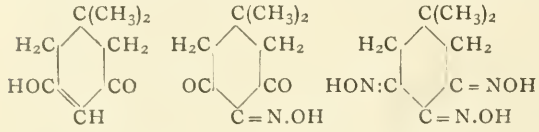


1-Keto-3-methyl-Δ^3-tetrahydrobenzene (Rabe, *Ber.*, 1907, xl., 2482)—

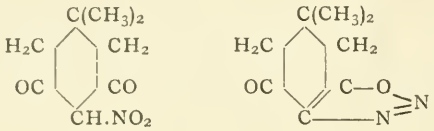


exists in two isomeric forms, which must have the same structure, as on oxidation with potassium permanganate both yield γ-acetobutyric acid. The molecular refraction would lead to the conclusion that both are doubly unsaturated alcohols and not ketonic in nature. Chemically the two forms are identical except in their behaviour towards ferric chloride, when the one gives a pale wine-red colour, whereas the other becomes violet. The present data do not suffice to explain this case of isomerism.

Dimethyldihydroresorcin (I.) reacts towards nitrous acid as a diketone (Haas, *Journ. Chem. Soc.*, 1907, xci., 1433), for the resulting isonitrosodimethyldihydroresorcin (II.) reacts with two molecular proportions of hydroxylamine to give a compound of Formula III. Oxides of nitrogen con-

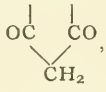


I. II. III.

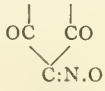


IV. V.

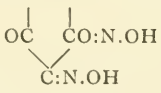
vert dimethyldihydroresorcin into the nitro-derivative (IV.), which substance, on reduction, yields an amine, and this gives with nitrous acid a compound whose constitution may be represented by Formula V. The relation of colour to constitution in these compounds is somewhat striking. Thus, while dimethyldihydroresorcin—



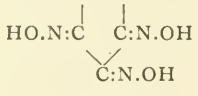
is colourless, isonitrosodimethyldihydroresorcin—



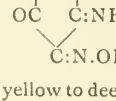
is yellow; its potassium and ferrous salts are deep blue, and its ammonium salt violet: the monoxime—



is colourless, but dissolves in alkalis to a yellow solution, and gives with ferrous sulphate a deep azure blue. The dioxime—

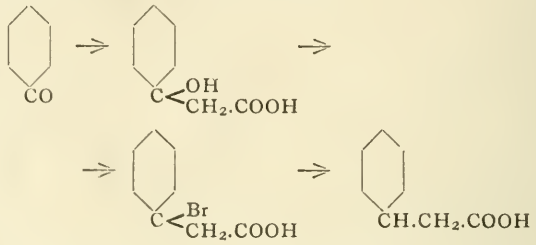


on the other hand, is greyish pink, but gives a yellow solution in caustic alkalis, and produces with ferrous sulphate a violet colour. Replacement of one of the carbonyl oxygen atoms in isonitrosodimethyldihydroresorcin by the imino group,—



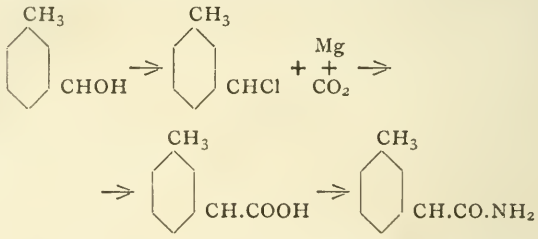
changes the colour from yellow to deep violet; the potassium salt of this compound is magenta, while the ferrous salt is deep blue.

Acids.—A number of carboxylic acids of the hydroaromatic series have been synthesised by Wallach (*Cent. Blatt.*, 1907, ii., 52) by condensing cyclic ketones with ethyl bromoacetate. The hydroxyl group in the resulting esters is replaced by bromine through the agency of hydrogen bromide, and the halogen free acids obtained by treatment with zinc and acetic acid.



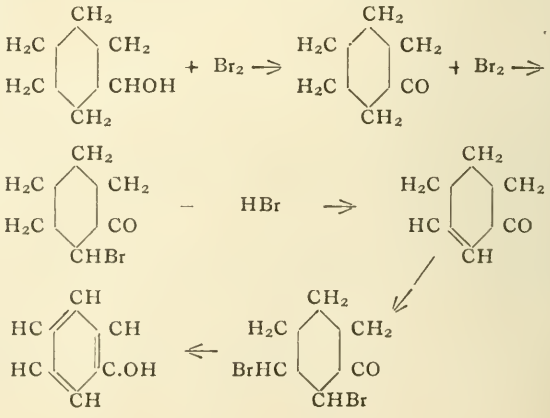
Skita (*Ber.*, 1907, xl., 4167) concludes from a study of ethyl 4-amino-2 : 6 : 6-trimethylhexahydrobenzene-1-carboxylate, prepared from ethyl isophoronecarboxylate, that hydroaromatic amino acids show *cis-trans* isomerism; that they are similar in their chemical behaviour to the aliphatic amino-acids, and also physiologically, in that they possess the property of producing local anæsthesia.

Amines.—Gutt (*Ber.*, 1907, xl., 2061) has prepared hexahydrobenzylamine and the five theoretically possible aminomethylhexahydrobenzenes, which are easily characterised by the melting-points of their benzoyl derivatives. The preparation is realised as follows :—



On treatment with bromine in presence of sodium methoxide the amide gives a urethane, which on distillation with lime yields the amine.

Aromatic from Hydroaromatic Substances.—Kötz and Götz (*Annalen*, 1908, cccIviii., 183) have studied the action of chlorine or bromine on hydroxyhexahydrobenzene and on hexahydrosalicylic acid, and have isolated a number of products intermediate between the fully saturated hydroaromatic bodies and the corresponding aromatic derivatives. An indication of the course of the various reactions may be gleaned from the following scheme :—



Reference may also be made to the following papers, which contain a description of many interesting hydroaromatic substances:—"Hydroaromatic Sulphur Compounds" (Borsche and Lange, *Ber.*, 1907, xl., 2220), "Hydrophthalic Acids" (Abati, *Journ. Chem. Soc.* Abst., 1907, i., 419), "Synthesis of Alcohols of the Hexahydrobenzene Series" (Sabatier and Mailhe, *Ann. Chim. Phys.*, 1907, [8], x., 527), "Derivatives of Phenylcyclohexane" (Kursanow, *Journ. Chem. Soc.* Abst., 1907. i., 599), "Hexahydrobenzaldehyde" (Zelinsky and Gutt, *Ber.*, 1907, xl., 3050, 3055).

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

Part III.—Analysis of the Aluminium and Iron Groups, including Beryllium, Uranium, Vanadium, Titanium, Zirconium, and Thallium.

By ARTHUR A. NOYES, WILLIAM C. BRAY, and ELLWOOD B. SPEAR.

(Continued from p. 229).

Confirmatory Experiments and References (continued).

Action of H_2S *on Molybdate dissolved in excess of* NH_4OH. — A solution containing 6 mgrms. Mo as $(NH_4)_2MoO_4$ and 4 cc. HCl (1·12) in 30 cc. was treated by P. 51: no precipitate formed with NH_4OH, nor with $(NH_4)_2S$. To the nearly colourless filtrate were added 5 cc. NH_4OH (0·90), and H_2S was led through the solution in a test-tube for twenty minutes: after three minutes the solution was dark yellow, after five minutes it had a reddish colour, after ten minutes it was brilliant red, and the colour did not change in the next ten minutes. The colour was not the same as in the case of vanadium, but might be mistaken for it if a comparative test were not made. 50 mgrms. Mo as $(NH_4)_2MoO_4$ and 3 grms. NH_4Cl were dissolved in 100 cc. water, 5 cc. NH_4OH (0·90) were added, and the solution was saturated with H_2S: the colours obtained were the same as in the preceding experiment. The last experiment was repeated with 1 mgrm. Mo: the solution finally became deep orange in colour.

Action of Acids on Sulphomolybdate.—50 mgrms. Mo as $(NH_4)_2MoO_4$, 3 grms. NH_4Cl, and 5 cc. NH_4OH (0·90) were dissolved in 100 cc. water, and saturated with H_2S. The red solution was filtered and then made distinctly acid with acetic acid: the colour remained nearly the same; on filtering, a very small black precipitate was obtained which contained less than 1 mgrm. Mo. The solution was allowed to stand for one hour: it remained clear. After three hours a small precipitate had separated which contained only 2 or 3 mgrms. Mo. The mixture was then boiled for five minutes and filtered: about two-thirds of the molybdenum precipitated as MoS_3, and the filtrate was still deep orange. The filtrate was evaporated to a small volume, and 10 cc. HCl (1·20) added: a large black precipitate of MoS_3 separated, but the solution was found to still contain 1 or 2 mgrms. Mo.

The foregoing experiment was repeated, except that HCl was added to the cold solution: a large black precipitate separated at once. The filtrate was evaporated to 30 cc. and tested for Mo by *P. 43*e*: none was found. The experiment was repeated except that the mixture was boiled after adding HCl: the result was the same, not more than a trace of molybdenum being found in the filtrate.

P. 52, N. 3: *The Formation of Sulphate on dissolving* NiS *in Acids.*—In two experiments 300 mgrms. Ni as freshly precipitated NiS were treated by P. 52, the sulphur was filtered off, and $BaCl_2$ was added to the filtrate: small precipitates of $BaSO_4$ separated, each of which was estimated to contain 5 to 10 mgrms. Ba. In another series of experiments the NiS was first treated in the cold for several minutes with mixtures of 5 cc. HNO_3 (1·20) with 20 to 20 cc. water, and the residue was dissolved by evaporating the solution to concentrate the HNO_3, and then adding a few drops HCl (1·20): precipitates of $BaSO_4$ resulted, estimated to contain 20 to 50 mgrms. Ba. In each of these experiments, and especially when the precipitate was first treated with HNO_3, considerable sulphur separated, and the NiS enclosed in it did not dissolve readily.

P. 52, N. 4: *Action of* HCl *on Titanium and Zirconium Hydroxides.*—Acid solutions containing 100 mgrms. Ti and 100 mgrms. Zr as chlorides in volumes of about 100 cc. were treated in the cold with NH_4OH; the precipitates were filtered off and treated with 20 cc. cold HCl (1·12): they dissolved completely in a minute or two. The experiments were repeated, except that the solutions were heated to boiling, and the NH_4OH was added to the hot solutions: on pouring 20 cc. HCl (1·12) repeatedly through the filters containing the hydroxide precipitates, almost all of the $TiO(OH)_2$ dissolved, but only a small portion of the $ZrO(OH)_2$ (8 to 10 mgrms. Zr). On pouring a 20 cc. portion of hot HCl (1·12) repeatedly through the filters, the remainder of the titanium, but only about half the zirconium, dissolved. The remainder of the $ZrO(OH)_2$ was boiled in a casserole with HCl (1·12) for several minutes: it dissolved completely.

P. 52, N. 5: *Complete Precipitation of Titanium and Zirconium in the Sodium Peroxide Procedure.*—1 mgrm. Ti as $TiCl_4$ was treated with NaOH and Na_2O_2 by P. 52, the mixture being boiled for about four minutes after the Na_2O_2 was added: a white precipitate separated. The filtrate was made acid with HCl; one-half of it was tested for titanium by adding H_2O_2: no colour appeared, showing that the titanium had been completely precipitated. The other half of the filtrate was tested for H_2O_2 by adding excess of $TiCl_4$: no colour appeared, showing that the Na_2O_2 had been completely decomposed. The experiment was repeated with 500 mgrms. Ti: the filtrate contained 1 or 2 mgrms. Ti. The precipitate was treated with HCl (1·12): nearly all dissolved in the cold, and the remainder on warming. The solution was reddish yellow, showing that the precipitate contained some TiO_3. The HCl solution obtained in the last experiment (containing nearly 500 mgrms. Ti) was treated with NaOH and Na_2O_2 by P. 52; the mixture containing Na_2O_2 was boiled for less than one minute: the filtrate contained at least 5 mgrms. Ti. These experiments show that the amount of titanium that remains in the filtrate may be greatly lessened by long continued boiling.

1 mgrm. Zr as $ZrCl_4$ was treated with NaOH and Na_2O_2 by P. 52: a distinct precipitate separated. The experiment was repeated with 100 mgrms. Zr; the large precipitate was filtered off, and the filtrate was tested for zirconium by acidifying with HNO_3, evaporating almost to dryness, and adding Na_2HPO_4 solution: only a trifling precipitate separated, thus proving that the precipitation of the zirconium had been complete.

Action of NaOH *on Uranyl Salts.*—A solution containing 5 mgrms. U as UO_2Cl_2 and a little HCl in 15 cc. was neutralised with 10 per cent NaOH solution, and an excess of 2 or 3 cc. was added: a small yellowish precipitate separated. This was filtered off and the filtrate was tested for uranium by acidifying and adding NH_4OH: a small precipitate separated, which was estimated to contain 2 or 3 mgrms. U. The experiment was repeated, except that the mixture containing NaOH was boiled for a minute or two: nearly all of the precipitate which had formed in the cold was re-dissolved. Therefore the uranium is not completely precipitated by a small excess of NaOH. 50 mgrms. U as $UO_2(NO_3)_2$ were added to 30 cc. 10 per cent NaOH solution, and the mixture was heated to boiling, cooled, and poured through a hardened filter; half of the filtrate was tested for uranium as above: only a small precipitate of $(NH_4)_2U_2O_2$ separated, showing

* From the *Journal of the American Chemical Society*, xxx., No. 4.

that the uranium had been nearly completely precipitated by the alkali.

Composition of Sodium Aluminate, Zincate, Beryllate, and Chromite.—For the evidence that sodium aluminate in solution has the formula $Na^+AlO_2^-$, see Noyes and Whitney (*Zeit. Phys. Chem.*, 1894, xv., 694); Hantzsch (*Zeit. Anorg. Chem.*, 1902, xxx., 296). Hantzsch has shown by means of conductivity measurements that a solution of the empirical composition Na_3AlO_3 contains mainly NaOH and $NaAlO_2$, and some colloidal $Al(OH)_3$.

Hantzsch (*Zeit. Anorg. Chem.*, 1902, xxx., 298, 303) concluded from conductivity measurements that a 1/200 molal solution of sodium zincate, even in the presence of a sevenfold excess of NaOH, is almost completely hydrolysed into NaOH and $Zn(OH)_2$, and that the latter is present as a colloid. Fisher and Herz (*Zeit. Anorg. Chem.*, 1902, xxxi., 355) confirmed this by dialysis experiments. Kunchert (*Zeit. Anorg. Chem.*, 1904, xli., 343), working with a larger excess of alkali, and using Bodländer's electromotive force method, proved, however, that the solutions contained chiefly $ZnO_2^=$ and some $HZnO_2^-$. Forster (*Zeit. Elektrochem.*, 1899, vi., 301) has prepared solid $NaHZnO_2$.

Hantzsch (*loc. cit.*) concludes that H_2BeO_2 is a very weak acid, weaker than $HAlO_2$, but much stronger than H_2ZnO_2.

From dialysis and conductivity experiments Fisher and Herz (*loc. cit.*) conclude that in alkaline chromite solutions chromium is present almost solely as colloidal $Cr(OH)_3$.

Behaviour of Cobalt Hydroxide towards NaOH.—See Donath (*Zeit. Anal. Chem.*, 1901, xl., 137).—An acid solution containing 100 mgrms. Co as nitrate in 30 cc. was neutralised with 10 per cent NaOH and an excess of 15 cc. added; 2 grms. Na_2O_2 were added a little at a time to the cold solution, the mixture was boiled for two or three minutes, cooled, and filtered: the filtrate had a deep blue colour. It was acidified, made alkaline with NH_4OH, and H_2S was passed into it: a precipitate separated which was estimated to contain 5 to 8 mgrms. Co. The experiment was repeated, except that no excess of NaOH was added: the filtrate was colourless and no cobalt was found in it. This last experiment was repeated except that 4·5 grms. Na_2O_2 were used instead of 2 grms.: again the filtrate contained no cobalt. Therefore the blue (soluble) cobalt compound is formed only by the action of concentrated alkali on a *cobaltous* salt, and the cobalt is completely precipitated if it is first oxidised to the cobaltic state by Na_2O_2 in a weakly alkaline solution.

The first experiment with the large excess of NaOH was repeated with 100 mgrms. Ni instead of Co: no nickel was found in the filtrate.

P. 52, N. 6: *Formation of Peruranates.*—See P. Melikow and L. Pissarjewsky (*Zeit. Phys. Chem.*, 1899, xxviii., 556). A large number of salts are known in the solid state; *e.g.*, $UO_4.2Na_2O_2.8H_2O$; $UO_4.2BaO_2.8H_2O$; $UO_4.2BaO_2.10H_2O$; &c. The salts of the alkali elements are soluble in water, the others insoluble. These salts may be regarded as compounds of peruranic anhydride, UO_4, with peroxides of the other elements. They were prepared by the action of H_2O_2 on solutions of uranyl salts in the presence of the hydroxides of the other elements.

A HNO_3 solution containing 100 mgrms. U as $UO_2(NO_3)_2$ in 25 cc. was treated by P. 52: the solution was yellow when acid, and a yellow precipitate separated on adding NaOH; on adding Na_2O_2 (3 grms.) and boiling, a deep red solution resulted. This solution was acidified with HNO_3: it became yellow. To a portion of it was added a little $TiCl_4$ in HCl solution: an orange-red colour resulted, proving the presence of free H_2O_2. Therefore the uranium is oxidised by Na_2O_2 to a soluble "peruranate," which is stable in the strong alkali, but apparently decomposes readily in the acid solution with formation of H_2O_2 and a uranyl salt. The experiment was repeated, except that only about 0·5 grm. Na_2O_2 was added: a yellow uranium precipitate remained, but the solution contained a large proportion of the uranium.

P. 52, N. 7: *Complete Decomposition of* Na_2O_2 *by Boiling.*—2 grms. Na_2O_2 were added to a neutral solution containing 0·5 grm. NaCl in 30 cc., the mixture was heated to boiling, boiled for one minute, cooled, acidified with HNO_3, and tested with $TiCl_4$ solution for H_2O_2; the solution remained colourless. The experiment was repeated with 100 mgrms. Mn as $MnCl_2$, the MnO_2 being filtered off before the filtrate was made acid: it contained no H_2O_2. The experiment was repeated with 100 mgrms. V as Na_3VO_4: the result was the same. See the preceding paragraph as to the effect of uranium.

Precipitation of Thallium by Sodium Peroxide.—1, 3, and 20 mgrms. Tl as $Tl(NO_3)_3$ were treated in separate experiments by P. 52: brown precipitates separated in each case on adding NaOH, and remained after the treatment with Na_2O_2. The solutions, which were filtered off almost immediately after diluting, were found to contain about 0·5, 1, and 2 to 3 mgrms. respectively. 1 mgrm. Tl as Tl_2SO_4 was treated by P. 52: no precipitate separated on adding NaOH; there was a slight coloration on adding Na_2O_2, but no precipitate remained upon boiling; when, however, the solution was set aside to cool, a good precipitate separated in ten or fifteen minutes, and the filtrate was found to contain only 0·2 to 0·4 mgrm. Tl. A mixture containing 1 mgrm. Tl as TlCl, 200 mgrms. Fe as $FeCl_2$, 200 mgrms. Mn as $MnCl_2$, and 200 mgrms. Al as $AlCl_3$ was treated by P. 52: the filtrate was evaporated nearly to dryness and tested for thallium by *P. 65*d*: no precipitate of TlI separated.

P. 52, N. 8: *Necessity of Adding* Na_2CO_3 *to Precipitate Barium.*—1 and 2 mgrms. Ba as $BaCl_2$ were treated by P. 52, the final volume being about 30 cc.: on boiling, a precipitate which was proved to contain barium appeared in both experiments, but it was very slight in that with 1 mgrm. These experiments were repeated, except that no Na_2CO_3 was added: no precipitate appeared on boiling.

2 mgrms. Cr and 100 mgrms. Ba as chlorides were treated by P. 52, except that no Na_2CO_3 was added: the filtrate was colourless, and the solution obtained on dissolving the precipitate in HNO_3 was yellow, showing that the chromium had been precipitated as $BaCrO_4$. The experiment was repeated with 1 mgrm. Cr and 100 mgrms. Ba, except that Na_2CO_3 was added: the filtrate was yellow, showing that the addition of Na_2CO_3 causes chromium to pass into the filtrate even when a large amount of barium is present.

Solubility of Zinc Carbonate in NaOH.—50 mgrms. Zn as nitrate were dissolved in 20 cc. water and an equivalent amount of Na_2CO_3 added: a white precipitate separated. 5 cc. more 10 per cent NaOH solution were added: the precipitate dissolved. 5 cc. more NaOH and 10 cc. 10 per cent Na_2CO_3 solution were added, and the mixture heated to boiling: no precipitate separated. More Na_2CO_3 was added: a precipitate finally formed.

P. 52, N. 9: *Solubility of the Phosphates of Aluminium and Zinc in* NaOH.—100 mgrms. Zn and 100 mgrms. Al as phosphates were dissolved in separate experiments in 25 cc. water and a very little HNO_3 (1·20); 10 per cent NaOH was added slowly: precipitates separated but dissolved when an excess of about 4 cc. had been added.

Partial Decomposition of Phosphates on Treating with Sodium Hydroxide.—50 mgrms. Mg, 50 mgrms. Ca, and 20 mgrms. (ferric) Fe, all as freshly precipitated phosphates, were boiled separately with about 30 cc. 4 per cent NaOH solution for three or four minutes in covered casseroles; the mixtures were filtered, the precipitates being washed with dilute NaOH. The filtrates were made strongly acid with HNO_3, and the precipitates were dissolved in HNO_3. Each solution was evaporated to a small volume and treated with several cc. ammonium molybdate solution. The amount of phosphate in each solution was estimated by the amount of yellow precipitate

that had separated out after several hours: in the case of magnesium only a very small proportion of the phosphate remained in the precipitate; in the case of the iron about one-fifth remained in the precipitate; and in the case of calcium the phosphate was about equally divided between precipitate and filtrate.

Behaviour of Calcium Borate and Oxalate towards Sodium Hydroxide.—A mixture containing 100 mgrms. Ca as $CaCl_2$ and 80 mgrms. BO_2 as H_3BO_3 was treated by P. 52: the precipitate was tested for borate by adding to it in a casserole H_2SO_4 (1·84) and alcohol, igniting the alcohol and stirring vigorously: no green colour appeared. The filtrate was acidified with H_2SO_4, evaporated, and tested in the same way: a large amount of borate was found. A trial experiment showed that 5 mgrms. BO_2 could easily be detected in this way.

A mixture containing 500 mgrms. Fe as $FeCl_3$, 500 mgrms. C_2O_4 as oxalic acid, and 100 mgrms. Ca as $CaCl_2$ was treated by P. 52; the filtrate was analysed for oxalate by acidifying, adding NH_4OH and $CaCl_2$: a very large precipitate of calcium oxalate separated. The experiment was repeated with 300 mgrms. Ca and 500 mgrms. C_2O_4 (but no iron): the result was the same. The precipitate was tested for oxalate by dissolving it in HCl and adding NH_4OH: a small precipitate separated, showing that a large proportion of the oxalate had passed into the filtrate.

Decomposition of Oxalic Acid by Acids.—10 and 100 mgrms. oxalic acid were treated separately by P. 61, about 1 grm. $KClO_3$ being added to the concentrated HNO_3 solution. The solutions were finally evaporated to almost 5 cc., diluted to 30 cc., neutralised with NH_4OH, and tested for oxalate by adding 10 cc. of 10 per cent $Ca(NO_3)_2$ solution: no precipitate separated in either experiment. The experiment with 10 mgrms. oxalic acid was repeated, except that no $KClO_3$ was added to the HNO_3 solution: a precipitate containing about 3 mgrms. oxalic acid resulted. 10 mgrms. oxalic acid were added to 15 cc. HCl (1·20), the mixture was evaporated to 2 or 3 cc., diluted and tested for oxalic acid as above: a precipitate of calcium oxalate separated that was estimated to correspond to 3 or 4 mgrms. oxalic acid. The experiment was repeated with aqua regia instead of HCl (1·20): somewhat more oxalic acid was decomposed, but at least 2 mgrms. remained. These experiments prove that the decomposition of oxalic acid is very rapid in a hot mixture of HNO_3 and $HClO_3$, much slower in aqua regia, and still slower in HCl (1·20) or HNO_3 (1·42).

P. 52, N. 10: *Colour of an Alkaline Solution of Sodium Chromate and Peruranate.*—1 mgrm. Cr as $KCrSO_4$ was treated by P. 52, the final volume being about 30 cc.: the yellow colour of the solution was easily seen.

1 mgrm. U as $UO_2(NO_3)_2$ was treated by P. 52, the final volume being about 15 cc.: the solution was distinctly yellow. The experiment was repeated with 5 mgrms. U; the solution had a reddish tinge. It was diluted to 30 cc.: the reddish colour changed to yellow.

(To be continued).

Lectures on Forensic Chemistry.—Mr. W. Jago, F.I.C., of Lincoln's Inn, Barrister-at-Law, will deliver a course of four public lectures on Forensic Chemistry at University College. The first lecture will be given on Friday, November 13th, at 5.30, when the chair will be taken by Mr. A. J. Walter, K.C. The Lectures are open to the public without fee or ticket.

Honours.—The Royal University of Ireland have conferred the degree of D.Sc. *honoris causa* on Prof. Alfred Senier, of Queen's College, Galway, in recognition of his services as a teacher of chemistry in Ireland, and of his researches in organic chemistry, notably his work on acridines.

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

The following complete the abstracts of Papers received during the vacation, and published or passed for publication in the *Transactions*:—

184. "*The Interaction of the Metals of the Aluminium Group and Organic Halogen Derivatives.*" By James Frederick Spencer and Marion L. Wallace.

Aluminium, indium, and thallium react directly with both aromatic and aliphatic halogen derivatives on heating. In the case of the chloro-derivatives and the lower aliphatic compounds (up to butane), heating in a sealed tube was necessary to bring about the reaction. The formation of an intermediate aluminium organic halide, similar to the Grignard compounds, is the primary result of this interaction, and this compound is decomposed on the addition of water with the production of the parent hydrocarbon and the evolution of much heat. In some cases, the evolution of heat does not take place, and in these cases the parent hydrocarbon is present in the mixture before the addition of water. In all such cases the reactions are extremely slow, it being necessary to heat the substances for twenty-four to thirty hours before the reaction is complete; so that in all probability the intermediate compound is formed, and then decomposed by the atmospheric moisture. The indium and thallium reactions, of which only few have been studied, proceed very slowly, as, indeed, do also some of the aluminium reactions, but certain of the latter take place with extreme violence. The yield of hydrocarbons varies from 25 to 75 per cent of the theoretical. In a few cases, the reaction proceeds along a second line, namely, the formation of a hydrocarbon or derivative containing double the number of carbon atoms as the original substance. The best examples of this are the formation of dimethyl succinate from methyl bromoacetate, and the formation of benzidine from bromoaniline by the action of aluminium. In no case could a reaction between these metals and the halide derivatives be brought about in ethereal solution.

185. "*The Relation between Unsaturation and Optical Activity.* Part IV. *The Relative Influence of Bi-, Quadri-, and Sexavalent Sulphur on Rotatory Power.*" By Thomas Percy Hilditch. (*Trans.*, 1908, 1618).

The optical activity of derivatives of *l*-amyl alcohol and *d*-camphor containing sulphur of all the above degrees of valency has been compared, and it has been found that a bi- or quadri-valent sulphur atom has a larger effect on optical rotatory power than saturated sexavalent sulphur, and, also, that the optical anomaly is enhanced by the presence of a second unsaturated group adjacent to the sulphur residue. The maximum change of rotatory power appears to take place when two identical unsaturated groups occur in conjugation, as in the disulphides.

In addition, the study of a series of active salts of corresponding sulphinic and sulphonic acids shows that the sulphonic acid exerts a greater influence on the rotatory power of the base, and this agrees with the effect of unsaturation observed in other cases, on the assumption that the sulphinic salts contain sexavalent sulphur.

186. "*Oxidations of Hydrocarbons of the Benzene Series.* Part II. *Substances containing a Negative Radicle.*" By Herbert Drake Law and Frederick Mollwo Perkin. (*Trans.*, 1908, 1633).

The authors have investigated the oxidation of the nitrotoluenes with chromyl dichloride. Contrary to Etard's statement that quinones are produced, *p*- and *m*-nitrotoluene give good yields of the corresponding aldehydes. With *o*-nitrotoluene, no aldehyde is formed, but a chlorinated compound of no definite boiling-point. With *o*-, *m*-, and *p*-chlorotoluenes, the corresponding aldehydes are in all cases obtained. Diphenylmethane yields diphenylcarbinol,

and triphenylmethane gives triphenylcarbinol; in both cases in practically theoretical yields. Naphthalene, anthracene, and fluorene were also oxidised, but definite products were not obtained.

187. "*Coprosterol.*" (Part I.). By Charles Dorée and John Addymann Gardner. (*Trans.*, 1908, 1625).

Having shown that cats and dogs when fed on a raw brain diet produce coprosterol in considerable amount, the authors have studied the action of oxidising and isomerising agents on the substance. Coprosterol is readily oxidised by chromic acid to a ketone, *coprostanone*, which crystallises in leaves melting at 62—63°. The *semicarbazone* melts at 192°, and the *oxime* at 69°. Coprostanone forms with phenylhydrazine a crystalline substance melting at 191°, to which a formula has not yet been assigned. When heated with sodium amyl-oxide, coprosterol is converted into *ψ-coprosterol*, melting at 119°, and yielding an *acetate*, m. p. 83°, and a *benzoate*, m. p. 85°, which differ from the corresponding derivatives of coprosterol. On oxidation with chromic acid, however, it yields the same ketone, coprostanone.

188. "*The Spontaneous Crystallisation of Solutions of some Alkali Nitrates.*" By Bernard Mouat Jones. (*Trans.*, 1908, 1739).

The author has determined the temperatures of spontaneous crystallisation of supersaturated solutions of the nitrates of potassium, rubidium, and cæsium of various strengths. The method was that used by Hartley, Jones, and Hutchinson (*Trans.*, 1908, xciii., 825) in investigating sodium sulphate solutions. The effect of mechanical friction was studied by introducing fragments of Jena glass into the tubes before sealing. Crystalline fragments, such as garnet, were not used, in order to avoid possible unequal "inoculating" effects on the three solutions. The temperatures at which supersaturated solutions of the salts in question would crystallise spontaneously when slowly cooled and constantly shaken have been recorded. Temperatures corresponding with tubes containing glass fragments lie on regular curves, namely, the supersolubility curves, above which crystallisation cannot take place in the absence of crystal nuclei. Tubes containing no glass fragments generally needed to be cooled into the labile region before crystallisation would occur. The supersolubility curves for potassium and rubidium nitrates run nearly parallel to the solubility curves, approaching the latter as the concentration decreases. For cæsium nitrate, the solubility and supersolubility curves coincide, the metastable region disappearing.

The three corresponding ice-supersolubility curves have been traced, and also the ice-solubility curves for dilute solutions of rubidium and cæsium nitrates. The spontaneous production of the ice phase seems to be a somewhat less definite phenomenon than the production of the salt phase.

Although the order of molecular solubility is rubidium nitrate, potassium nitrate, cæsium nitrate, the order for the sizes of the metastable ranges follows that of the molecular weights, that for potassium nitrate being greatest, and that for cæsium nitrate least. For example, for a concentration of 0·6 grm.-mol. of salt to 100 grms. of water, the metastable ranges are approximately 4°, 1°, and 0° respectively.

189. "*Syntheses with Phenol Derivatives containing a Mobile Nitro-group.* Part I. *The Interaction of 2 : 3 : 5-Trinitro-4-acetylaminophenol and Amines.*" By Raphael Meldola and James Gordon Hay. (*Trans.*, 1908, 1659).

The trinitroacetylaminophenol referred to was described by one of the authors in 1906 (*Trans.*, lxxxix., 1935), and its great reactivity due to the mobility of the 3-nitro group, indicated in that paper. The compound has now been submitted to further investigation, more especially with reference to the formation of iminazoles from amines. In the present paper, the authors consider the mechanism of the formation of iminazoles in connection with the conditions that determine the mobility of the nitro-group on the one hand, and, on the other, the nature of the amine with which the trinitro-compound is brought into combination. A quantitative method for determining the yield of iminazole has been devised, and complete series of determinations have been carried out with the isomeric chloroanilines, nitroanilines, and anisidines. The results bring out very clearly the influence of steric hindrance in the case of ortho-substituted amines, the nitro-group being so completely protective that no combination takes place with methylaniline, benzylaniline, diphenylamine, or carbazole. A number of new iminazoles have been prepared, and are described in the paper.

190. "*The Constituents of the Expressed Oil of Nutmeg.*" By Frederick Belding Power and Arthur Henry Salway. (*Trans.*, 1908, 1653).

Ceylon nutmegs, of good quality, yielded on expression 26·6 per cent of oil, and when completely extracted with ether, 42·9 per cent of oil was obtained. The constants of the expressed oil and of the total fatty acids were as follows :—

	Expressed oil.	Total fatty acids.
Melting-point	48°	49°
Density, 50°/50° ..	0·9399	0·9012
Acid value	11·2	218·3
Saponification value .	174·6	—
Iodine value	57·8	23·1

The composition of the expressed oil or fat was approximately as follows :—Essential oil, 12·5 per cent; trimyristin, 73·0 per cent; oleic acid, as glyceride, 3·0 per cent; linolenic acid, as glyceride, 0·5 per cent; formic, acetic, and cerotic acids, very small amounts; unsaponifiable constituents, 8·5 per cent; resinous material, 2·0 per cent.

The chief unsaponifiable constituent was a new *compound*, $C_{18}H_{22}O_5$, amounting to about 5 per cent of the expressed oil. It is a yellow, transparent, extremely viscid liquid (b. p. 270—280°/15 mm.), and is devoid of any marked physiological action. The remainder of the unsaponifiable material consisted of myristicin, $C_{11}H_{12}O_3$, with a little phytosterol, $C_{20}H_{34}O$ (m. p. 134—135°).

191. "*The Preparation of Disulphides.* Part IV. *Esters of Dithiodiglycollic and Dithiodilactylic Acids.*" By Thomas Slater Price and Douglas Frank Twiss. (*Trans.*, 1908, 1645).

On submitting the mixture obtained by the interaction of ethyl bromoacetate and sodium thiosulphate in aqueous-alcoholic solution to electrolysis in the cathode compartment of a divided cell, diethyl dithiodiglycollate separates as a heavy oil; from methyl bromoacetate the dimethyl ester is obtained. In a similar manner, the diethyl esters of α-dithio- and β-dithio-dilactylic acids were prepared from ethyl α-bromopropionate and ethyl β-iodopropionate respectively. These esters are all fairly mobile liquids, heavier than water, and possessing a peculiar odour which is not very disagreeable, and not at all like that which is usually associated with the liquid mercaptans and disulphides. The boiling-points of these esters are as follows: —*Dimethyl dithiodiglycollate*, 154°/14 mm.; *diethyl dithiodiglycollate*, 164°/14 mm.; *diethyl α-dithiodilactylate*, 159°/14 mm.; *diethyl β-dithiodilactylate*, 194°/17 mm.

For complete identification of these esters, the corresponding acids were prepared from them by hydrolysis with hydrochloric acid. The properties of the acids obtained agreed with those found by previous observers.

192. "*Contributions to the Chemistry of the Cholesterol Group.* Part I. *The Action of Hydrogen Peroxide and of Fused Potassium Hydroxide on Cholesterol.*" By Robert Howson Pickard and Joseph Yates. (*Trans.*, 1908, 1678).

A detailed account of work, of which a preliminary

account has already appeared (*Proc. Chem. Soc.*, xxiv., 121).

193. "*Derivatives of* S-*Phenylphenazothionium.*" (Part II.). By Samuel Smiles and Thomas Percy Hilditch. (*Trans.*, 1908, 1687).

Further proof of the constitution of these substances is now offered from a general standpoint. Condensation of phenol with di-*p*-nitrodiphenylamine sulphoxide yields the sulphates of two isomeric S-hydroxyphenylphenazothionium bases, which are distinguished by their different solubilities and colours in various media. The reduction products of the dinitro-S-phenetyl and -hydroxyphenyl derivatives have also been prepared; these on oxidation yield blue dye-stuffs similar to thionine. *iso*Dinitrodiphenylamine sulphoxide yields similar derivatives, which are distinguished from those of the di-*p*-nitro-series by greater solubility and absence of fluorescence.

194. "*The Trithionates and Tetrathionates of the Alkali Metals.*" (Part I.). By John Edwin Mackenzie and Hugh Marshall. (*Trans.*, 1908, 1726).

The authors have prepared a number of tetrathionates from persulphates and thiosulphates (compare Marshall, *Journ. Soc. Chem. Ind.*, 1897, xvi., 396), thus, $2SrS_2O_3 + K_2S_2O_8 = K_2S_4O_6 + 2SrSO_4$, and of trithionates by removal of sulphur, thus,—

$$K_2S_4O_6 + K_2SO_3 = K_2S_3O_6 + K_2S_2O_3.$$

The crystallographic details of some of the salts are as follows:—

Potassium trithionate, $K_2S_3O_6$. Rhombic, bipyramidal. $a : b : c = 0{\cdot}7168 : 1 : 0{\cdot}4193$. Refractive indices: $\alpha = 1{\cdot}4925$, $\beta = 1{\cdot}5646$, $\gamma = 1{\cdot}6014$. Calculated axial angle, $2V = 68° 15'$. Density, 2·336. Molecular volume, 115·8.

Rubidium trithionate, $Rb_2S_3O_6$; isomorphous with the above. $a : b : c = 0{\cdot}7058 : 1 : 1{\cdot}04176$. Refractive indices: $\alpha = 1{\cdot}4874$, $\beta = 1{\cdot}5580$, $\gamma = 1{\cdot}5867$. Calculated axial angle, $2V = 62° 23'$. Density, 2·845. Molecular volume, 127·7.

Cæsium trithionate, $Cs_2S_3O_6$, is not isomorphous with the above. Triclinic. Density greater than 3·326.

Cæsium trithionate monohydrate, $Cs_2S_3O_6,H_2O$. Triclinic. Density, 3·192. Molecular volume, 149·1.

The authors find that rubidium and cæsium can be estimated by conversion into the double sulphate of calcium and the alkali metal.

195. "*The Synthesis of Complex Acridines.*" By Percy Corlett Austin. (*Trans.*, 1908, 1760).

The author has applied the methods employed by Senier and himself in the synthesis of various phenonaphthacridines and dinaphthacridines (*Trans.*, 1906, lxxxix., 1387; 1907, xci., 1233, 1240; 1908, xciii., 63) to the synthesis of acridines derived from phenanthrene and the closely-allied fluorene. A phenophenanthracridine has also been prepared by the condensation of phenanthraquinone and *o*-nitrobenzyl chloride in the presence of stannous chloride. This is an adaptation of Baezner's reaction (*Ber.*, 1904, xxxvii., 3077).

Diphenanthracridine, $C_{14}H_8\langle{}^{N}_{CH}\rangle C_{14}H_8$, is a yellow crystalline substance, insoluble in most solvents; it can be distilled under diminished pressure, and re-crystallised from nitrobenzene. Its melting-point is above 320°.

Phenophenanthracridine, $C_{14}H_8\langle{}^{N}_{CH}\rangle C_6H_4$, is prepared by treating an alcoholic solution of a mixture of phenanthraquinone and stannous chloride with *o*-nitrobenzyl chloride. After distillation under diminished pressure, it crystallises from benzene in yellow crystals, melting at 204°.

Fluorene-$\langle{}^{N\text{-}\alpha}_{CH\text{-}\beta}$*-naphthacridine*, $C_{13}H_8\langle{}^{N}_{CH}\rangle C_{10}H_6$, is prepared from 2-aminofluorene and α-naphthol by the action of methylene di-iodide. After distillation under diminished pressure and re-crystallisation from toluene, it melts at 259°.

A brown powder is also obtained by the action of methylene di-iodide on 2-aminofluorene, but no method was found for the purification of this substance.

196. "*A Reaction Distinguishing Phosphoprotein from Nucleoprotein, and the Distribution of Phosphoproteins in Tissues.*" By Robert Henry Aders Plimmer and Frederick Hughes Scott. (*Trans.*, 1908, 1699).

In 1906, Plimmer and Bayliss (*Journ. Physiol.*, xxxiii., 439) found that the phosphorus of caseinogen was completely eliminated as phosphoric acid by the action of 1 per cent aqueous sodium hydroxide at 37° in twenty-four hours.

The phosphorus of vitellin, the other well-defined phosphoprotein, is eliminated as phosphoric acid under the same conditions, but the phosphorus of nucleic acid, lecithin, and glycerophosphoric acid, the other phosphorus-containing substances in the tissues, is not separated in this way.

The reaction thus serves as a simple means of distinguishing phosphoproteins from nucleoproteins, and it permits of the determination of the presence of phosphoproteins which are stated to occur in various tissues.

As phosphates are present in all tissues, the reaction cannot be applied directly, but by first extracting the fats and lecithin with alcohol and ether, dissolving out the phosphates from the coagulated protein with water acidified with hydrochloric acid, and then treating it with 1 per cent aqueous sodium hydroxide at 37°, the presence of phosphoprotein can be demonstrated. By this procedure, a determination of the amount of the various kinds of phosphorus compounds in the tissues can also be made.

The pancreas alone of the tissues examined contained phosphoprotein, the amount of phosphorus present in this form being about 3 per cent of the total phosphorus.

Ichthulin, the protein contained in caviar, the eggs of the sturgeon, is described as a phosphoprotein. Its nature has been confirmed by this method, and phosphoproteins have also been found in the eggs of the herring and mullet.

The principal distribution of phosphoproteins is thus in those substances which form the food-stuffs of the embryo bird and fish and the young mammal.

197. "*The Colouring Matters of the Stilbene Group.* Part V. *The Action of Caustic Alkalis on Derivatives of Para-nitrotoluene.*" By Arthur George Green and James Baddiley. (*Trans.*, 1908, 1721).

Derivatives of *p*-nitrotoluene containing as ortho-substituent electro-positive or weakly electro-negative groups (CH_3, OMe, or CO_2H), react least readily with caustic alkalis, giving red intermediate compounds, and on oxidation, derivatives of dinitrodibenzyl. By carrying the combined condensation and oxidation further, the dinitrodibenzyl derivatives are finally converted into dinitrostilbene derivatives, apparently by intermediate formation of nitronitrososstilbenes:—

$$\begin{array}{l} CH_2{\cdot}C_6H_4{\cdot}NO_2 \\ | \\ CH_2{\cdot}C_6H_4{\cdot}NO_2 \end{array} \xrightarrow[\text{Condensation}]{} \begin{array}{l} CH{\cdot}C_6H_4{\cdot}NO \\ \| \\ CH{\cdot}C_6H_4{\cdot}NO_2 \end{array} \xrightarrow[\text{Oxidation}]{} \begin{array}{l} CH{\cdot}C_6H_4{\cdot}NO_2 \\ \| \\ CH{\cdot}C_6H_4{\cdot}NO_2 \end{array}.$$

On the other hand, 2 : 4-dinitroluene, like other derivatives of *p*-nitrotoluene with a strongly electro-negative ortho-substituent (CN, SO_3Ph, &c.), is far more reactive, giving an excessively unstable blue intermediate product, which is oxidised to tetranitrostilbene without the formation of any dibenzyl compound. The conclusion is drawn that the red intermediate products are nitronitrosodibenzyl derivatives, whilst the blue intermediate compounds are dinitrososstilbene derivatives, both classes of nitroso-compounds existing in an alkaline solution in the form of quinonoid alkali salts.

4 : 4′-*Dinitro*-2 : 2′-*dimethylstilbene*, obtained from *p*-nitro-*o*-xylene, forms yellow needles, which melt at 288—290°. 4 : 4′-*Dinitro*-2 : 2′-*dimethoxystilbene*, prepared from *p*-nitro-*o*-cresol methyl ether, crystallises in orange needles, melting at 268—269°. 4 : 4′-*Dinitrostilbene*-2 : 2′-*dicarboxylic acid*, obtained from nitro-*o*-toluic acid, crystallises from cresol in pale yellow crystals, which melt and decompose at 288—291°. 2 : 4 : 2′ : 4′-Tetranitrostilbene is formed by the action of cold alcoholic potash and iodine on 2 : 4-dinitrotoluene. 2 : 4 : 2′ : 4′-Tetra-aminostilbene forms pale yellow leaflets, which melt at 183—186° (Echales, *Ber.*, 1904, xxxvii., 3599, gives 191° or below).

198. "*The Solubility of Lime in Water.*" By Gerald Tattersall Moody and Lewis Thomas Leyson.

The widely divergent numbers giving the solubility of lime in water recorded by previous observers are to be ascribed to the use of impure lime, and to faulty methods of determining the solubility. The observed difference in the solubility of lime obtained from different sources is not ascribable to any peculiarity of the lime itself, but is due to the presence of impurities which either affect the solubility of the lime or are capable of neutralising acids, thereby causing an error wherever the lime present in solution is estimated by titration with acid.

An apparatus specially devised for eliminating the errors in method made by previous observers has allowed figures showing the solubility of lime between 2° and 80° to be obtained, and it is found that the curve of solubility between 25° and 80° is practically a straight line.

PHYSICAL SOCIETY.

Ordinary Meeting, October 23rd, 1908.

The meeting was held at the National Physical Laboratory, Bushy House, Teddington, by kind invitation of the Director. All departments of the Laboratory were thrown open for inspection, and, in addition, a number of special demonstrations had been arranged.

In the Engineering Department Dr. Stanton described a new Fatigue Testing Machine for Metals. For comparison, one of the earliest types of fatigue testing machines—viz., that used by Wöhler—was shown. Here alternations of stress are produced by the rotation of a loaded cantilever. This method is only useful at low speeds.

The new machine is suitable for very great changes in speed, and lends itself to a determination of the effect of rapidity of reversals on the life of the specimen. The test-piece, in the form of a short hollow cylinder, is placed between three rollers, the upper one of which is loaded by a lever and weights. The rollers are supported on friction wheels. The maximum stresses occur on the inside of the ring, the variation being from a maximum tension at the points of contact with the rollers to a maximum compression midway between. There are therefore three cycles of stress for each revolution of the specimen, and no difficulty is found in imposing 2500 cycles per minute at a moderate speed of rotation of the rollers.

Mr. Bairstow showed a Single-lever Testing-machine for producing alternations of direct stress, specially designed with compound knife-edges so that the change from tension to compression can be made by moving the jockey. The extensions of the specimen are observed at intervals on a Marten's Extensometer. The rate of reversals is necessarily low, being only about 100 per hour. The object of the experiments is to determine the elastic range under variation of stress.

In the Electro-technical Department Mr. Paterson and Mr. Rayner showed the appliances and arrangements for testing alternating-current instruments. The method of calibrating the Electrostatic Wattmeter on alternating current was explained. In connection with this work standard resistances were shown giving a two-volt drop with currents of 1000 to 2000 amperes.

A demonstration was also given of the procedure followed in carrying out life tests of electric glow-lamps in accordance with the specification drawn up by the Engineering Standards Committee. The method of setting up lamps at a standard value of watts per candle was shown, as well as the arrangements for determining and regulating the voltage of lamps under life test. The equipment includes a new and specially designed photometer on the substitution principle.

In the Metallurgy Department Mr. Rosenhain exhibited the process of quenching metals *in vacuo* in the ingeniously simple apparatus devised by him. The specimen is heated in a silica tube-furnace, connected at one end through a large receiver to the air-pump, and at the other through a stopcock to a tube dipping under water to a measured depth. On opening the stopcock the water rushes through as far as the receiver only, "quenching" the specimen, and washing it along to the colder parts of the silica tube.

Mr. Rosenhain also showed the ultra-violet apparatus for photomicrography which has been installed at the Laboratory. The difficulty of focussing which always obtains is greatly increased in the use of the apparatus for metallurgical work, owing to the small amount of light which appears to be obtainable by reflection from the surface of metal specimens. The method adopted, which involves the use of monochromatic blue light, with auxiliary lenses, preceding the transfer to the ultra-violet rays obtained from cadmium electrodes, was explained, and some excellent photographs were shown obtained at a magnification of 400 diameters.

In the Electricity Department Mr. Campbell showed the measurement of small self-inductances down to a few tenths of a microhenry. The apparatus is arranged so that tests can be made either at low or high frequency (100 and 2000 $\frown\!\!\smile$ per sec. respectively). In the first case a wire interrupter and a vibration galvanometer are used, and in the second a microphone hummer. A tuned telephone apparatus for the absolute measurement of the high frequencies used in wireless telegraphy was also shown. It consists of the usual arrangements for producing high frequency oscillations, and a special camera with a quickly rotating mirror, by which photographs of the oscillatory sparks can be obtained.

In the new Metrology Building Mr. Jeffcott showed the apparatus employed for the various measurements of length, comparisons and calibration of scales, comparison of end gauges with the standards, measurements of screws, &c. Of special interest may be mentioned the Hartmann automatic comparator, which compares two end gauges, automatically recording the readings on a revolving drum, with a magnification of 2000. The gauges are themselves automatically interchanged. The Pratt and Whitney machine for comparing end gauges was also shown, fitted with a Newell spirit-level as a contact indicator, enabling differences to be measured to 0·00001 inch. The building has been designed specially to accommodate a 50 metre comparator for the verification of surveying tapes and wires, both on the flat and in catenary, and the erection of this apparatus will shortly be completed.

In the Thermometry Department the main new feature was the newly equipped room for the testing of mercury thermometers. The old chemical laboratory has been adapted for this purpose.

A series of special comparison-tanks, designed by Dr. Harker and Mr. W A. Price, has been installed on an iron railing running down the centre of the room. They are each fitted with electric heating and a system of pipes for hot and cold water supply, automatic overflow and waste, and are stirred continuously by a suitable motor.

The electric heating is so arranged for all ordinary purposes that the requisite energy can be obtained for maintaining a constant or slowly rising or falling temperature, without the use of large and expensive series resistances, while 2500 watts is available in each bath for rapid heating, between the individual sets of comparisons.

Ice and steam baths of various types, and oil and nitrate baths for high temperature work are also installed.

In the new electric-furnace room a large furnace equipment for the testing of optical pyrometers was shown in action though not yet complete. The pyrometers, carried on a massive rotating support, can be successively brought under the mouth of a furnace giving "black-body" radiation at temperatures up to 1400° C., the furnace temperature being measured by appropriate thermo-couples. A similar furnace for much higher temperatures is in preparation to be fitted in a second cell on the same elevated platform. Various types of instruments and furnaces were exhibited, and the apparatus employed by Messrs. Harker and Sexton in their determination of the effect of pressure on the sulphur boiling-point was shown in action by Mr. Sexton.

CORRESPONDENCE.

WOMEN AND THE FELLOWSHIP OF THE CHEMICAL SOCIETY.

To the Editor of the Chemical News.

Sir,—We venture to ask for the hospitality of your columns in order to make a statement of some importance, in view of the announcement made by the President of the Chemical Society of the large majority of the Fellows who are in favour of the admission of women to the Society (*Proc. Chem. Soc.*, xxiv., 203).

Four years ago a memorial was presented to the Council of the Chemical Society praying for the admission of women to the Fellowship of the Society. This memorial bore the signatures of nineteen women, all of whom were lecturers or demonstrators in chemistry in university colleges, or actively engaged in original chemical investigations. The Council at that time were unable to take any steps in the matter, but promised that the memorial should not be lost sight of in any further action that might be taken (*Proc. Chem. Soc.*, 1905, xxi., 103).

The question having been raised again by the presentation of a petition signed by 312 Fellows in June last, we communicated in July with our co-signatories of the 1904 memorial, and with other women of equal repute as chemists, in order to ascertain how many women at the present time desire the privileges afforded by Fellowship of the Chemical Society.

We have received replies from twenty-eight women, all of whom are of similar standing and possessing similar qualifications to the original signatories, expressing their interest in the present movement and their intention of at once becoming candidates for admission to the Fellowship of the Chemical Society if the Council should reach a favourable decision in this matter.

From rumours that have reached us, there appears to be some uncertainty in the minds of some Fellows of the Society as to the number of women who are prepared to avail themselves of the first opportunity of seeking the Fellowship, and we hope that the publication of the above statement will remove all misunderstanding on this point.—We are, &c.,

Ida Smedley,
M. A. Whiteley.

November 9th, 1908.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvii., No. 14, October 5, 1908.

Microchemical Reactions of Arsenic Applicable in Forensic Chemistry. — G. Denigès. — A drop of the arsenical solution is slowly evaporated to dryness. The diameter of the drop must not exceed 5 mm. The residue is allowed to cool, and a drop of reagent is deposited on it; after three minutes the preparation is examined under the microscope. With ammoniacal silver nitrate red rhombic or hexagonal crystals are obtained; with acetic acid and silver nitrate crystals derived from a rhomboid dodecahedron are observed, while with magnesia mixture crystals in the shape of an X or like fern leaves are formed. If the process is performed exactly according to the directions given by the author this method may be used to obtain very characteristic crystals with traces of arsenical products present as arsenic acid.

Active Pinonic and Pinic Acids.—Ph. Barbier and V. Grignard.—The oxidation of *l*-pinene by potassium permanganate gives *l*-pinonic acid of formula $C_{10}H_{16}O_3$. When treated with hydroxylamine chlorhydrate and potash in aqueous solution it is transformed into a mixture of oximes, one dextro- and the other lævo-rotatory, which can easily be separated by taking advantage of their different solubilities in ether. By the oxidation of *l*-pinonic acid with sodium hypochlorite or hypobromite an oily acid is obtained, the formula of which is $C_9H_{14}O_4$. It is dextro-rotatory, and appears to be *d*-pinic acid. *D*-pinene on oxidation gives a mixture of *d*-pinonic acid and the racemic acid, the constituents of which may be separated by crystallisation in a mixture of ether and ligroin, in which the racemic acid is only slightly soluble. By oxidising the *d*-acid the same *d*- and *l*-oximes are obtained. These researches show that the acid obtained by Tiemann by oxidising sodium *a*-campholenate, and by distilling a-dioxy-dihydrocampholenic acid, and described as *l*-pinonic acid, is not the true *l*-acid derived from *l*-pinene. It differs from it in melting-point, in the melting-point of its oxime, and in the products of oxidation. Possibly these two *l*-acids are the *cis* and *cis-trans*-isomers, the existence of which is foretold by theory.

Determination of Succinic Acid in Presence of Fixed Acids in Wines and Fermented Liquids.—Emm. Pozzi-Escot. — A known volume of liquid is neutralised by ammonia and acidified with a slight excess of acetic acid, and then barium chloride is added to precipitate oxalic and mineral acids. The liquid is filtered and the filtrate is boiled; excess of lead acetate is then added to precipitate albumenoids, tannins, &c., which are separated off by filtration. The filtrate is treated with sulphuric acid, then with sulphuretted hydrogen, filtered and boiled to expel excess of sulphuretted hydrogen. To separate the malic and succinic acids in the solution it is acidified with sulphuric acid and oxidised with potassium permanganate. The succinic acid remains in the solution, which is boiled; a little potassium bisulphite is added and a large excess of barium chloride to remove the sulphuric acid. The filtered liquid is concentrated, ammonia, alcoholic barium bromide, and three volumes of alcohol are added, and thus barium succinate is precipitated. This is ignited in a muffle, and the barium carbonate determined by titrating with decinormal hydrochloric acid.

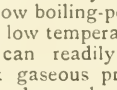
No. 15, October 12, 1908.

Method of Calculating Atomic Weights. — Louis Dubreuil.—The experimental errors which may occur in atomic weight determinations are of three kinds. (1) Errors due to the method employed; (2) errors due to the technique of the experimenter; (3) accidental errors. These last may easily be eliminated by taking the mean of a great number of experiments. The elimination of the others is much more difficult. The method of calculation used since the time of Berzelius consists in considering the atomic weights of the elements implicated in an experiment as known, except one which is calculated as a function of the others; thus the first two classes of errors are accumulated in the result. Hinrichs has recently established an important relation for the calculation of the atomic weights, which, however, is affected by a small error. Taking this

relation as a basis the author has eliminated the small error by deducing the variations of the true values of the atomic weights from the values usually adopted.

MISCELLANEOUS.

Ozonides of Simple Olefines.—C. Harries and Karl Haeffner.—Gaseous olefines explode when they come in contact with ozone, even at a very low temperature. But if the hydrocarbons of low boiling-point are diluted with a solvent which boils at a low temperature and is indifferent towards ozone, they can readily be transformed into ozonides. To convert gaseous propylene into ozonide ethyl chloride may be used as solvent, and by a modification of the method the ozonide of ethylene can, no doubt, be prepared. The ozonides are stable oils; the propylene compound crystallises at a low temperature. They may be distilled *in vacuo* without undergoing decomposition, though the operation is dangerous as slight superheating leads to an explosion. Two modifications of the ozonides appear to exist, one a thick oil and the other a mobile liquid; the latter results when the first form is distilled or heated in a vacuum. The two forms differ in refractive index and specific gravity. They do not appear to be polymers, but the thick oil seems to contain more oxygen than the other form, which is the normal ozonide. The values obtained for the molecular refraction and dispersion seem to show that the three oxygen atoms are not bound as shown by the formula—



but that one oxygen forms part of a carbonyl group, and two others are ether oxygens.—*Berichte*, xli., No. 13.

MEETINGS FOR THE WEEK.

Friday, 13th.—Physical, 5 (at the Physics Laboratory, University College, Gower Street, by kind invitation of Prof. F. T. Trouton, F.R.S.). "The Photo-electric Properties of Potassium-sodium Alloys," by J. A. Fleming. "Re-combination of Ions in Air," by P. Phillips. "Influence of Magnetic Field on the Photographic Patterns produced by the Electric Spark" and Exhibition of an Experiment Illustrating an Anomalous Effect of Lagging Thin Wires, by A. W. Porter. "Rate of Growth of Viscosity in Congealing Solutions," by A. O. Rankine. "Isomers of Adsorption by Solid Surfaces from Solutions," by F. T. Trouton.

Wednesday, 18th.—Royal Society of Arts, 5. Inaugural Address of the 155th Session, by Sir William H. White, K.C.B., LL.D., F.R.S., Vice-President and Chairman of the Council.

Thursday, 19th.—Chemical, 8.30. "Meteloidine, a New Solanaceous Alkaloid," by F. L. Pyman and W. C. Reynolds. "Affinity of certain Alkaloids for Hydrochloric Acid" and "Affinity Constants of Bases as Determined by Methyl-orange," by V. H. Veley. "Relation between Absorption Spectra and Chemical Constitution—Part XII., Some Aminoaldehydes and Ketones of the Aromatic Series," by E. C. C. Baly and Miss E. G. Marsden. "Organic Derivatives of Silicon—Part VIII., The Resolution of *dl*-Sulphobenzylethylisobutylsilicyl Oxide and the Properties of the Optically Active Acids," by B. D. W. Luff and F. S. Kipping. "Study of the Constitution and Properties of the Rhodanides of Inorganic Radicles," by A. E. Dixon and J. Taylor. "Action of Phosphorus Pentachloride on the Methylene Ethers of Catechol Derivatives—III., The Cyclic Carbonates of Dichloro-ethyl- and Propyl-catechol," by G. Barger. "Synthesis of Thionaphthen Derivatives from Styrenes and Thionyl Chloride," by G. Barger and A. J. Ewins.

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THE CHEMICAL NEWS.

Vol. XCVIII., No. 2556.

A SIMPLE COLORIMETRIC METHOD FOR THE DETERMINATION OF FORMALIN IN MILK.

By E. W. T. JONES, F.I.C.

Reagent.—Dissolve 0·25 grm. of pure iron wire in HCl, oxidise with HNO_3, precipitate with ammonia, filter, well wash the precipitate, then dissolve it in 500 cc. of strong HCl.

Standard Formalin Solution.—Add 1 cc. of formalin (40 per cent CH_2O) to distilled water, and make to 1000 cc. 0·1 cc. of this from a 1 cc. pipette divided into tenths, added to 10 cc. of milk, equals 1 part of formalin in 100,000 parts of milk.

Procedure.—Put 10 cc. of the milk containing formalin into a large test-tube (1 inch by 6 inches), also put two more 10 cc. of pure milk into two other tubes; add to one of the latter 0·1 cc. and to the other 0·2 cc. of the dilute formalin solution; now add to each of the three tubes 10 cc. of the acid reagent, well mix, then put all the tubes simultaneously into water at 90° C. and keep at 80° to 85° C. for twenty to twenty-five minutes; then add 30 cc. of cold water to each tube, well shake, cool and throw on to filters; when through pour on to each of the filters about 10 cc. of cold distilled water, and when this is through make each of the blue filtrates to 100 cc. If the sample being tested, compared in a Nessler glass, gives a darker colour than the 0·1 cc. standard, it is better to dilute the 0·2 cc. standard to 200 cc., when 100 cc. will equal 0·1 cc., which is dark enough to use as a standard for comparison.

I find with only 0·1 cc. of the dilute formalin in 10 cc. of milk the colour is not so pure a blue as the diluted solution of a larger amount, and therefore for nesslerising the larger amounts it is better to dilute the stronger for a standard.

I do not describe the nesslerising because every laboratory assistant knows this procedure.

N.B.—The sample and the standards must be submitted to strictly the same conditions side by side.

I have obtained regularly most satisfactory results. The great advantage is that the determination can be made with only 10 cc. of milk in an hour or less, and I believe with greater accuracy than by the more troublesome distillation process requiring 100 cc. of milk.

Wolverhampton, October 30, 1908.

THE PRESENT STATE OF OUR KNOWLEDGE OF RADIO-ACTIVITY.*

By A. DEBIERNE.

(Continued from p. 236).

III.

We have seen that radio-active substances are characterised by the spontaneous emission of a special radiation; I shall now describe the principal properties of this radiation.

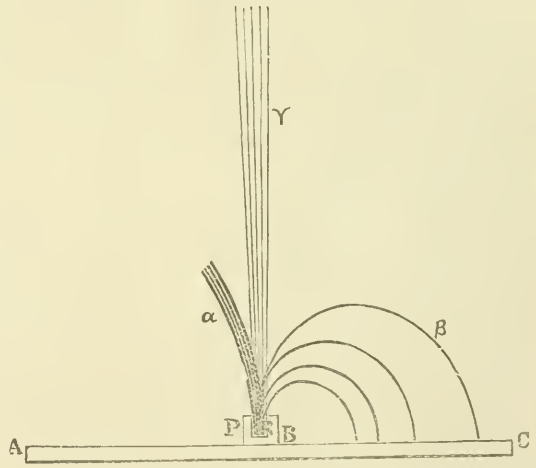
The complexity of the radiation emitted by radium salts was shown by the experiments of Becquerel, P. Curie and Mdme. Curie, Rutherford, Villard, &c. It is possible to distinguish different kinds of rays, which may be compared to those obtained by an electric discharge in a Crookes tube.

The existence of three kinds of rays has been been proved in this tube—cathode rays, which are normally projected from the negative electrode; canal rays, which are found behind the cathode, when the latter is perforated; and Röntgen rays or X-rays, which are emitted chiefly by a sheet of metal, called the anticathode, placed in front of the cathode. It has been shown that the cathode rays are composed of particles much smaller than the atoms, and negatively charged; they are called electrons. The velocity of these particles is of the order 100,000 km. per second. The canal rays are formed of much larger particles, postively charged, and having a rather smaller velocity. Finally, the Röntgen rays are not electrified; they appear to be a peculiar disturbance in the ether produced every time an electron with a high velocity is suddenly stopped by a solid substance.

The rays emitted by active substances may also be grouped in three classes:—The α-rays, positively electrified, and analogous to the canal rays; β-rays, negatively electrified and analogous to the cathode rays, and the γ-rays, non-electrified and analogous to the Röntgen rays.

The electric charges emitted by the radium rays were first directly determined by Pierre Curie and Mdme. Curie.

The distinction between the different kinds of rays could be established by different methods. Firstly, their different powers of penetrating matter could be employed. The α-rays have the least penetrating power; they are completely absorbed by a layer of air a few centimetres thick



or by a sheet of aluminium one-thirtieth mm. thick. β-Rays of different penetrations are known, but, in general, they are much less penetrating than α-rays; some of them can pass through aluminium 1 cm. thick. Finally, the γ-rays have very great power of penetration, and it has been shown that they are not completely absorbed by a screen of lead several cm. thick.

The different kinds of rays may also be distinguished by the action of a magnetic field. For the projection of electrified particles may be compared with an electric current, and an intense magnetic field may exert on the moving particles a force great enough to modify their trajectory. The β-rays are the most sensitive to the action of the magnetic field; the α-rays undergo a much smaller deviation for the same field, and in the opposite direction. The γ-rays are not affected. The action of a magnetic field upon a pencil consisting of the three kinds of rays may be illustrated as in Fig. 1. The magnetic field produced by a field magnet, for example, being normal to the plane of the paper and directed towards this plane, the α-rays are slightly deflected to the left, and the β-rays are strongly deflected towards the right.

The trajectory of the electrified particles of the α- and β-rays can also be modified by an electric field, as, for example, by making them pass between the plates of an

* *Revue Générale des Sciences*, 1908, xix., 691.

air condenser, but the deviation obtained is always very slight. The α-rays are, of course, attracted towards the negatively charged plate and the β-rays towards the positively charged plate.

It may easily be shown that the electric and magnetic deviations must depend on the electric charge on each particle, on its mass, and its velocity; if for a certain kind of rays the deviations in a field of known intensity are measured, the velocity of the electrified particle can be calculated, and also the ratio e/m of the charge on a particle to its mass m.

These measurements have been made for the different kinds of rays. The measurements for the β-rays have been made chiefly by H. Becquerel and Kauffmann. They have shown that the β-radiation emitted by radium includes rays of very different velocities, from a velocity about half that of light to a velocity nearly equal to that of light; *i.e.*, 300,000 km. per second.

According to Kauffmann's experiments the most rapid rays give a value of e/m considerably smaller than that corresponding to the less rapid rays. The latter value appears to be identical with the value of e/m for the cathode rays, the velocity of which is still smaller. In modern theories of the nature of electricity, an interpretation of the greatest importance has been placed upon the variation of the ratio e/m with the velocity of the β-particle, for it has been shown that the material aspects of the electron—motion, inertia, kinetic energy—can be explained perfectly by considering only the electric charge in rapid motion in the ether, and that the apparent mass which results from this motion would increase rapidly when the velocity approached that of light. According to all the experiments which have been performed the β-ray must be regarded as a cathode ray of great velocity produced by an electron in rapid motion.

Measurements of the magnetic and electric deviations of the α-rays have been made chiefly by Rutherford. They show, to a first approximation, that all the α-particles have the same value for e/m in the rays emitted by different active substances — radium, thorium, actinium, and polonium—and if it is allowed that the electric charge e is equal, and of opposite sign to that of the electron, the mass of each particle is twice that of an atom of hydrogen.

As I have mentioned, the γ-rays do not suffer any deflection by a magnetic or electric field.

The different kinds of rays may cause the phosphorescence of certain substances—salts of the alkalis and alkaline earths, glass, barium platinocyanide, zinc sulphide, certain minerals, willemite, kunzite, diamond, &c., and also certain organic substances, paper and cotton. I have recently shown that the skin of the hands also becomes luminous under the action of radium rays. However, all these substances are not equally sensitive to the different rays; thus, barium platinocyanide is very sensitive to the γ-rays and zinc sulphide to the α-rays. The phosphorescence of zinc sulphide under the action of the α-rays exhibits a very curious phenomenon. When the phosphorescent substance, which has been subjected to the rays, is examined by the aid of a magnifying glass, it is seen that it is not uniformly luminous, but that there are on its surface numbers of little luminous points which appear and disappear very rapidly; thus an impression is produced of a multitude of little sparks on the zinc sulphide. It is thought that each little luminous point is produced by the bombardment of an α-particle, and attempts have been made to determine the number of particles emitted per second by an active substance by observing the number of luminous points which appear in the same time on a zinc sulphide screen. However this may be, this phenomenon of scintillation appears to be a characteristic property of the α-rays.

The path of the different kinds of rays can be followed by observing the phosphorescence, and thus the deviation in a magnetic field, and also the passage of the rays through different screens can be determined.

The path of the rays can be determined more exactly by using the photographic plate. This method, which was specially employed by Becquerel, enables us to verify the shape of the path of the β-rays in a magnetic field and various other properties.

The α-, β-, and γ-rays ionise gases, *i.e.*, they make them conductors by generating throughout them positive and negative charges, which move in an electric field; by the ionisation produced in a gas the intensity of the radiation of an active substance can be measured. The α-rays generally produce the greatest ionisation; as these rays are very easily absorbed, it follows that ionisation by an acive substance is greatly diminished by a screen, even at very thin one. The absorption of the rays by matter has been the subject of much important work which has given very interesting results, especially for the α-rays.

In the first place, it has been proved by Mdme. Curie that in air the α-rays have a range which comes to an abrupt end, and that at a certain distance from the active substance α-rays can no longer be detected. For instance, with polonium they disappear at 4 cm. and with radium at 7 cm. Bragg and Kleemann have studied this phenomenon, and have suggested a very satisfactory theory to account for it.

They have shown that every active substance (and we shall see further on that a great number of active substances must be supposed to exist) emits α-particles of the same kind and having the same velocity. If the active substance were infinitely thin, all the particles would have exactly the same range in air; this range is a quantity which is characteristic of the kind of α-rays and also of the nature of the active substance.

Rutherford has shown that the phenomenon of scintillation and photographic action cease at the same distance as the ionisation of a gas, and that at this distance the velocity of the α-particle is more than 40 per cent of its original value.

Finally, it must be mentioned that besides the rays previously described certain active substances emit electrons with very low velocities, and that the β- and γ-rays, when they impinge on matter, cause the emission by it of secondary rays analogous to those which the Röntgen rays produce.

IV.

Before discussing new phenomena the study of which has led to present-day theories of radio-activity, I must give an account of the general hypothesis, made at the beginning of their researches by Pierre Curie and Mdme. Curie, to explain the peculiar properties of radio-active substances.

The principal point to explain is the spontaneous and continuous emission of energy; and as we shall see presently, the quantity of energy emitted is much larger than might at first be supposed.

The two following hypotheses have been proposed :—

In the first hypothesis it is supposed that the energy is supplied from external sources in the form of a special radiation. This radiation, the nature of which is unknown, would cause in radio-active substances a phenomenon analogous to that which is produced with phosphorescent substances; it would be absorbed by the active substance, and its energy given back to the surroundings in the form of α-, β-, and γ-rays, &c.

In the second hypothesis it is supposed that the energy is derived from the active substance itself; the emission of energy must then be accompanied by a modification of the substance. Pierre Curie and Mdme. Curie, who had demonstrated the atomic nature of the new property, made the bold supposition, even before the discovery of radium, that in this case the transformation would take place in the radio-active atom itself, which would thus undergo a veritable transmutation yielding different atoms. One of the most important consequences was also pointed out, *i.e.*, the progressive disappearance of the radio-active element, which would give place to other elements.

This hypothesis of atomic disintegration also explains the emission of material particles having high velocities.

It is not impossible to combine the two hypotheses and to suppose that an atomic transformation occurs, produced by an external agency of unknown nature acting continuously on the active substance.

As is well known, the hypothesis of atomic transmutation is the most fruitful, and has served as the basis for modern theories.

(To be continued).

JUBILEE OF PROFESSOR SAKURAI.

Professor Sakurai completed the twenty-fifth year of his professoriate in the Tokyo University last year, and this event has recently been made an occasion of public celebration by his friends and former pupils, who among other things have raised a considerable sum of money to be used as a fund for the encouragement of chemical research in association with his name and under the direction of the Tokyo Chemical Society. A volume of papers embodying scientific work recently done by some of his former pupils, together with those by Professors Kuhara and Haga, have also been specially contributed on this occasion to celebrate Professor Sakurai's jubilee. From this volume we have much pleasure in reprinting two papers by Masataka Ogawa on some new elements. The first of these is given below.

PRELIMINARY NOTE ON A NEW ELEMENT IN THORIANITE.*

By MASATAKA OGAWA, Rigakushi.

While working on thorianite in University College, London, under Sir William Ramsay's direction a few years ago, an element believed to be new was met with in the iron group in the usual course of analysis, but, owing to the small quantity, its nature could not be fully established. The subject has been resumed since my return to Japan, and it has fortunately been found that the same element also occurs in other minerals, such as reinite and molybdenite, both found in this country. This somewhat incomplete paper is now published as a preliminary notice of the work, which is still going on.

Treatment of Thorianite.

Preparation of the Oxide.—Finely powdered thorianite was treated with boiling concentrated nitric acid and the solution decanted off, this process being repeated until the fresh nitric acid was no longer coloured yellow. The residue, amounting to about 3 per cent and now nearly free from the chief constituents of thorianite, viz., thorium, uranium, iron, and lead, was boiled with concentrated hydrochloric acid, by which treatment a considerable quantity of titanium and antimony passed into solution and was decanted off. The residue was then treated with hydrofluoric acid in the presence of concentrated sulphuric acid in order to remove the silica, and, after ignition and fusion with hydrogen potassium sulphate, the whole mass was dissolved in cold water.

On boiling the diluted solution, however, a slight turbidity occurred, which was found to be due to the separation of a basic titanium compound. Hydrogen sulphide was then passed through the filtered solution, and some brown precipitate thereby formed was filtered off. To the filtrate ammonia was added after oxidation with nitric acid, and the precipitate formed was dissolved in dilute hydrochloric acid. To this solution oxalic acid was added, which produced a small quantity of a white precipitate consisting of the oxalates of thorium, &c., and this was filtered off. Ammonia and ammonium sulphide were then added to the filtrate; the black precipitate thereby formed was dissolved in dilute hydrochloric acid and re-precipitated by ammonium sulphide in the presence of an excess of ammonium carbonate, thus keeping in solution any uranium which might still be present. The ammonium sulphide precipitate was again dissolved in dilute hydrochloric acid and re-precipitated by ammonia in the presence of an excess of ammonium chloride. The precipitate, consisting chiefly of the hydroxides of iron, aluminium, and zirconium, was dissolved in dilute hydrochloric acid, the solution nearly neutralised with sodium carbonate, and boiled after the addition of sodium thiosulphate. The precipitate now formed was dissolved in hot concentrated hydrochloric acid, the separated sulphur filtered off, and the solution re-precipitated by sodium thiosulphate, the usual precautions being taken.

The precipitate was once more dissolved in concentrated hydrochloric acid, and, after evaporating off the excess of the acid and heating with some sulphuric acid, a saturated solution of potassium sulphate was added to the solution. After standing for twenty-four hours, the double sulphate of zirconium and potassium, which was formed, was filtered off. The filtrate was evaporated to a small bulk, and the crystals formed of potassium sulphate and alum were removed. After mixing the greenish coloured mother-liquor with 90 per cent alcohol and filtering, ammonia was added to the solution, when a pale yellow precipitate, believed to consist of the hydroxide of the new element, was obtained.

Properties of the Oxide.—The hydroxide above obtained is insoluble in ammonium chloride. It dissolves in alkalis, but not so easily as aluminium hydroxide. On drying at 100°, it becomes nearly black, and on ignition it changes to a dark brown powder. The ignited oxide is insoluble in acids, even in hot concentrated sulphuric acid to which some hydrofluoric acid has been added. On fusion with hydrogen potassium sulphate, however, and extracting the fused mass with water, the oxide may again be brought to solution. On fusion with sodium carbonate and potassium nitrate, the oxide gives a green mass, having much the same appearance as that of an alkaline manganate. This dissolves in water and forms a green coloured solution, from which a current of carbonic acid produces a brown precipitate, soluble in hydrochloric acid.

A solution of the hydroxide in hydrochloric acid has a yellowish green colour and gives a chocolate-brown precipitate on boiling with sodium thiosulphate. The same solution gives a greenish black precipitate with ammonium sulphide, insoluble in an excess of the reagent, and a yellowish brown precipitate with potassium chromate, insoluble in acetic acid and quite different in appearance from that of lead chromate. Potassium iodide gives no precipitate.

The yield of the oxide was a few centigrms. from one kilgrm. of the mineral. The portion of the mineral soluble in nitric acid also yielded a small quantity of the oxide.

I had also in store all the ammonia precipitate separated from the crude hydrogen sulphide precipitate given by Sir William Ramsay. The whole of this precipitate was ignited and treated as if it had been the original mineral, and a little over one decigrm. of the oxide was obtained from this source.

Salts.—Several attempts have been made to get well crystallised salts, but thus far without success. After fusing the oxide with hydrogen potassium sulphate, dissolving the fused mass in water, precipitating the hydroxide by ammonia, dissolving the precipitate in different acids, and evaporating these solutions, very soluble imperfect crystals were, indeed, obtained; but these crystals change to basic insoluble compounds on treatment with water. Attempts to get well defined crystals of double salts, containing the element in question, also ended in failure.

Anhydrous Chloride.—The oxide was heated in a porcelain boat in a current of chlorine gas, saturated with the vapour of carbon tetrachloride. There was formed a

* *Journal of the College of Science, Imperial University, Tokyo, Japan*, vol. xxv., Article 15.

very slight white sublimate, the main portion of the product remaining in the boat as a white powder having a slightly yellow tinge. On continued heating at low redness, a pale green sublimate was formed; but it was very slow in formation and insignificant in amount.

The residue in the boat, doubtless consisting of the anhydrous chloride, became deep green on being moistened with water, and dissolved into a pale green solution on the addition of more water, acidified with nitric acid. A portion of the solution was tested for thorium with negative results.

Equivalent Weight.—(1) A known weight of the chloride, prepared as above and contained in a small tube, was dissolved in acidified water, precipitated by ammonia, and the precipitate was ignited and weighed as oxide. 0·1092 grm. of the chloride gave 0·0742 grm. of the oxide, from which the number 50·3 was calculated as the equivalent weight of the element. (2) The oxide was fused with hydrogen potassium sulphate, dissolved in water, and precipitated by ammonia. This precipitate was dissolved in dilute sulphuric acid, the solution evaporated to dryness, and heated over a sulphur-bath until the weight became constant. The residue was ignited and weighed as oxide. 0·1253 grm. of the sulphate gave 0·0747 grm. of the oxide, again leading to the value 50·3. (3) The chloride, of which 0·0652 grm. was taken, was dissolved in water, acidified with nitric acid, and precipitated by silver nitrate, which gave 0·1120 grm. of silver chloride, whence follows the number 48 as the equivalent weight of the element.

Judging from the mode of working, the properties of the oxide and the chloride, as well as from the equivalent weight, the element in question must be considered as hitherto unknown, and this view has been further confirmed by—

Spectroscopic Examinations.—The oxide was fused with sodium carbonate and potassium nitrate, the fused mass dissolved in water, and the brown precipitate, obtained by passing a current of carbonic acid through the solution, was dissolved in dilute hydrochloric acid, and subjected to spectroscopic examinations. The lines were not remarkably strong, but three lines could be observed in the green-blue part of the spectrum. There were no manganese lines. Of the three lines, the strongest was the one having the wave-length 4882, believed to be correct within 10 units. The other two lines could also be measured, but, owing to their feebleness, the statement of their wave-length is here reserved.

Examination of Reinite.

The finely powdered mineral was fused with a mixture of sodium carbonate and potassium nitrate, the fused mass treated with water, ferric oxide filtered off, and the filtrate was saturated with carbonic acid gas. A brown precipitate, containing a little iron and silica, but otherwise apparently the same as that obtained, under like conditions, from the oxide extracted from thorianite, was produced. This was dissolved in dilute hydrochloric acid, and examined spectroscopically. The spectrum was exactly the same as before, though other lines were observed in addition.

Another portion of the powdered mineral was digested with hot nitro-hydrochloric acid, until its brown colour was completely changed into yellow, the solution evaporated to dryness, and the residue extracted with water acidified with hydrochloric acid. The solution, separated from insoluble tungstic acid, was saturated with hydrogen sulphide, the black precipitate thereby formed was filtered off, and the filtrate, after evaporation and oxidation, was treated with ammonia. The hydroxides of the iron group thus precipitated were re-dissolved in dilute hydrochloric acid, boiled with sodium thiosulphate in order to remove iron, and the re-precipitated hydroxides were filtered and ignited. The ignited oxides were then heated in a current of chlorine gas and carbon tetrachloride vapour. A difficultly volatile chloride, apparently identical with that obtained from thorianite, was thus produced. Its spectrum, also, was exactly the same as before. The yield of the oxide was, however, very much better, about 1 decigrm. having been obtained from 200 grms. of the mineral.

Examination of Molybdenite.

The powdered mineral was roasted in air until sulphurous acid gas was no longer given off. The residue, which was yellow when hot and pale greenish yellow when cold, was digested with a dilute solution of ammonia. The portion insoluble in ammonia was then digested with dilute hydrochloric acid, and the solution filtered from some undecomposed portion of the mineral. The acid solution was nearly neutralised with ammonia, and, after saturation with ammonium chloride and on standing, a pale yellow precipitate was formed. The precipitate, apparently ammonium vanadate, was removed by filtration. To the yellowish green filtrate, hydrogen sulphide was passed to saturation, and the black precipitate thereby formed was filtered off. The filtrate was freed from hydrogen sulphide by boiling, and then ammonia and hydrogen peroxide were added. The precipitated hydroxides were re-dissolved in dilute hydrochloric acid and boiled, as before, with sodium thiosulphate in order to remove iron.

The re-precipitated hydroxides were filtered, ignited, and fused with a mixture of sodium carbonate and potassium nitrate, and the fused mass dissolved in water. After decomposing the solution with hydrochloric acid, ammonia gave only a slight turbidity, due apparently to the presence of a small quantity of aluminium. On reduction, however, with zinc and hydrochloric acid, the solution gave an abundant precipitate with ammonia in the presence of an excess of ammonium chloride. The spectrum of the hydroxide thus obtained and dissolved in hydrochloric acid showed the same lines as those observed in the case of thorianite and reinite. The zinc used for reduction was prepared by the electrolysis of a pure solution of zinc ammonium sulphate.

The ammoniacal solution obtained on treating the roasted mineral with ammonia was also found to contain a portion of the element in question originally existing in the mineral; for this solution, after acidification with acetic acid and the removal of molybdic acid as barium molybdate, gave no precipitate with ammonia, but, on reduction with zinc and hydrochloric acid, ammonia in the presence of ammonium chloride produced some precipitate from it, which, on examination, was found to be the same hydroxide as that obtained, under like conditions, from the hydrochloric acid solution of the roasted mineral.

Thorianite, Reinite, and Molybdenite.

It will be seen from what has been stated that the new element is contained in reinite and molybdenite, as well as in thorianite, and, although it cannot yet be definitely stated, it is almost certain that molybdenite contains it in even a larger proportion than reinite.

It may be remembered that Dr. E. H. Buchner, in the course of his analysis of thorianite, observed the precipitation of a small quantity of a black sulphide in the arsenic group and occurrence of two other unknown substances in the bismuth-cadmium group (Chemical News, 1906, xciv., 233). I have not only confirmed his observations with thorianite, but have also met with the same unknown substances in the course of my examination of reinite and molybdenite. It is a striking case of coincidence that the three different minerals should contain these same unknown substances, besides the new element which forms the subject of this paper.

Conclusions.

Thiorianite, reinite, and molybdenite contain, in common, a new element, which is characterised by the following properties:—

1. The hydroxide, precipitated by ammonia in the presence of an excess of ammonium chloride, has an almost white colour with a pale yellow tinge. It is soluble in alkalis, but not so readily as aluminium hydroxide.

2. On drying at 100°, it becomes nearly black. The

ignited oxide has a dark brown colour and is insoluble in acids, but becomes soluble in water, after fusion with hydrogen potassium sulphate.

3. A solution of the hydroxide in hydrochloric acid has a yellowish green colour, and gives a chocolate-brown precipitate on boiling with sodium thiosulphate.

4. When ammonium sulphide is added to a solution of the chloride a greenish black precipitate, insoluble in an excess of the reagent is formed.

5. A solution of the chloride, acidified with acetic acid, gives a yellowish brown precipitate with potassium chromate. Potassium iodide gives no precipitate.

6. On fusing the oxide with sodium carbonate and potassium nitrate, a green mass is obtained, soluble in water. This solution gives a brown precipitate on passing a current of carbonic acid gas, the precipitate readily dissolving in dilute hydrochloric acid.

7. After fusion in the above manner, neither ammonia nor ammonium sulphide gives any precipitate; but on acidifying the solution, to which ammonium sulphide has been added, with hydrochloric acid, a brown precipitate is formed.

8. After the reduction of the above solution with zinc and hydrochloric acid, ammonia in the presence of an excess of ammonium chloride again precipitates the hydroxide.

9. When the oxide is heated in a current of chlorine gas saturated with the vapour of carbon tetrachloride, a difficultly volatile anhydrous chloride is obtained, which dissolves in water to form a pale green solution.

10. The chloride gives a characteristic line, besides two other feebler lines, in the green-blue part of the spectrum, having a wave-length of 4882.

11. The equivalent weight of the element is about 50; this element probably filling the gap between molybdenum and ruthenium and having an atomic weight of about 100.

12. The element appears to exist in two degrees of oxidation. The lower oxide behaves as a basic oxide, and comes along with alumina in the ordinary course of analysis. Its separation from the latter is, indeed, very difficult, the conversion into the difficultly volatile chloride by heating in a current of chlorine gas and carbon tetrachloride vapour being, at present, the only means of separation. The higher oxide behaves as an acidic oxide, similar to molybdenum trioxide, and is reducible into the basic oxide by means of zinc and hydrochloric acid.

The name Nipponium, with the symbol Np, was once suggested by Sir William Ramsay, and this name will be provisionally employed to indicate the new element.

I cannot conclude without expressing my heartiest thanks to Sir William Ramsay for his kind assistance and advice, and for his generosity in supplying me with the valuable material for this research while I was working in his laboratory.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

Part III.—Analysis of the Aluminium and Iron Groups, including Beryllium, Uranium, Vanadium, Titanium, Zirconium, and Thallium.

By ARTHUR A. NOYES, WILLIAM C. BRAY, and ELLWOOD B. SPEAR.

(Continued from p. 241).

Confirmatory Experiments and References (continued).

Colour of Vanadium Solutions. — 100 mgrms. V as Na_3VO_4 were added to a little concentrated HCl, and the mixture was evaporated to a small volume: the solution was at first orange-yellow but turned greenish blue on evaporation with HCl, showing reduction of the vanadium to the quadrivalent state. Excess of concentrated HNO_3 was added and the mixture again evaporated to a small volume: the solution rapidly became yellow and the concentrated solution was deep red, doubtless owing to the presence of free vanadic acid (see below). On diluting to about 20 cc. it became yellow. The solution was neutralised with 10 per cent NaOH solution: a small yellow precipitate separated during the neutralisation, but dissolved on the addition of a little more NaOH; the alkaline solution was of a deeper yellow colour than the dilute HNO_3 solution. Na_2O_2 was added: no change was observed. The mixture was boiled for one minute: the solution became colourless. The solution was cooled and made acid with HNO_3: it became yellow, the colour being deepest at the neutral point. To a portion of this acid solution were added 50 mgrms. Ti as $TiCl_4$: no change in colour was observed, showing that the Na_2O_2 had been completely decomposed and that no pervanadate had remained in the alkaline solution after boiling. Düllberg (*Zeit. Phys. Chem.*, 1903, xlv., 172) considers that the yellow colour is due to $H_4V_6O_{17}\equiv$, an ion of the tetrabasic hexavanadic acid, $H_4V_6O_{17}$ (see C. E., *P58*a*, N. 6).

P. 52, N. 11: *Division of Zinc in the Sodium Peroxide Treatment.*—500 mgrms. Fe as $FeSO_4$ and 10 mgrms. Zn as $ZnCl_2$ were treated by P. 52, the final volume being about 30 cc.; the filtrate was tested for zinc by P. 53 and 57: only about 3 mgrms. Zn were found, showing that the remainder had been carried down with the $Fe(OH)_3$. The experiment was repeated with 5 mgrms. Zn as $ZnCl_2$: only a trace of zinc was found in the filtrate. The last experiment (with 5 mgrms. Zn) was repeated, except that a large excess of NaOH was added before the Na_2O_2: 1 to 2 mgrms. Zn were found in the filtrate. The precipitate of $Fe(OH)_3$ was analysed by P. 64, 66, 67: the remainder of the zinc was found.

500 mgrms. Mn as $MnCl_2$ and 10 mgrms. Zn as $ZnCl_2$ were treated by P. 52, and the filtrate was tested for zinc by P. 53 and 57: no zinc was found. The experiment was repeated with 20 mgrms. Zn: a very small precipitate of ZnS was obtained in P. 57 which contained less than 0·5 mgrm. Zn. On analysing the precipitate by P. 61, 64, 66, and 67 the zinc was found. Therefore nearly 20 mgrms. zinc may be completely carried down when 500 mgrms. Mn are present. The experiment was repeated with 10 mgrms. Zn, except that the acid solution was poured into a fairly concentrated NaOH solution in P. 52: about 0·3 mgrm. Zn was found in the filtrate, showing that a little zinc remains in the filtrate in this case.

For the fact that zinc is carried down with nickel and cobalt, see T. A., No. 140 to 143.

Separation of Vanadium from Manganese.—A mixture containing 250 mgrms. Mn as nitrate and 1 mgrm. V as Na_3VO_4 was treated by P. 52; the filtrate was tested for vanadium by *P. 58*e*: a very good test was obtained.

P. 53, N. 1: *Solubility of Zinc Phosphate, Carbonate, and Oxalate in Ammonium Hydroxide.*—100 mgrms. Zn as $ZnSO_4$ along with an equivalent amount of sodium phosphate, sodium carbonate, or oxalic acid were dissolved in separate experiments in about 30 cc. cold water and about 2 cc. HNO_3 (1·20). The solutions were neutralised with NH_4OH (0·96) and an excess of about 3 cc. added: clear solutions were obtained in each case.

P. 54, N. 1 to 3: *Confirmatory Test for Aluminium.*—See Knoevenagel (*Prakticum des Anorg. Chemikers*, p. 160).

0·5 mgrm. Al and 0·2 mgrm. Co as nitrates were treated by P. 54: the ash retained the form in which the filter-paper was rolled and had a brilliant blue colour. The experiment was repeated with 0·2 mgrm. Al and 0·1 mgrm. Co: the residue was distinctly blue. The experiment was repeated with 0·1 mgrm. Al and 0·1 mgrm. Co: no blue colour was apparent.

Effect of other Elements upon the Confirmatory Test for Aluminium.—0·5 mgrm. Al and 0·2 mgrm. Co as nitrates were treated by P. 54, except that 1 mgrm. Fe as $Fe(NO_3)_3$ was also added: the residue was brown. This experiment

* From the *Journal of the American Chemical Society*, xxx., No. 4.

was repeated with 1 mgrm. Al: the residue was partly blue. The experiment was repeated with 2 mgrms. Fe and 1 mgrm. Al: the blue colour could scarcely be distinguished.

The experiment with 0·5 Al was repeated in the presence of 1 mgrm. Be as $Be(NO_3)_2$: the residue was blue. The experiment was repeated with 5 mgrms. Be: a satisfactory test for aluminium was obtained. The experiment with 1 mgrm. Al was repeated in the presence of 5 mgrms. Be and also of 10 mgrms. Be as nitrate: a fair test for aluminium was obtained in the presence of 5 mgrms. Be, but none with 10 mgrms. Be. In the latter case the paper and ash disintegrated.

1 mgrm. Al as nitrate was treated by P. 54, in the presence of 1, 2, and 5 mgrms. U as $UO_2(NO_3)_2$ respectively: a slight test for aluminium was obtained in the first experiment, a very poor one in the second, and none in the third. The experiment was repeated with 0·5 Al and 1 mgrm. U: the test was very poor.

The experiment was repeated with 1 mgrm. Al and 5 mgrms. V as Na_3VO_4: the residue was distinctly blue.

0·5 mgrm. Al as $Al_2(PO_4)_3$ and 0·2 mgrm. Co as nitrate were treated by P. 54: the residue was blue.

1 mgrm. Al as nitrate was precipitated by adding to it $NaHCO_3$ solution and boiling. The precipitate was filtered off, washed once, and treated by P. 54: the ash fused together into a small mass and no blue colour was apparent. 1 mgrm. Al and about 5 mgrms. Na as nitrates were then treated by P. 54: the result was the same, showing that the failure in the first experiment had been due to the presence of a sodium salt.

50 mgrms. SiO_2 as Na_2SiO_3 were dissolved in about 2 cc. HNO_3 (1·20) and 30 cc. water, heated to boiling, and made alkaline with NH_4OH: the solution slowly became turbid, and a gelatinous precipitate separated. This was collected on a filter, washed, and a portion of hot HNO_3 (1·20) was poured through the filter two or three times: the silica did not dissolve. The HNO_3 solution was tested for aluminium by P. 54, 0·5 mgrm. Co as nitrate being added: the residue was black. The experiment was repeated except that 2 mgrms. Al as nitrate were also present: a fair test for aluminium was obtained.

P. 56, N. 1: *Test for Chromate with Hydrogen Peroxide.* or the constitution and properties of the perchromic acid, and of other perchromates, see Riesenfeld (*Ber.*, 1905, xxxviii., 1885, 3380, 4578, and 4068).

In a series of test-tubes, each of which contained 0·3 mgrm. Cr as K_2CrO_4, were placed 0, 0·5, 2, 5, 10, and 20 cc. HNO_3 (1·20); each solution was diluted to 20 cc.; 3 to 5 cc. ether and 2 cc. H_2O_2 (3 per cent) were added, and the solutions were shaken: in the solution containing no acid, and in the solutions containing 5, 10, and 20 cc. acid, no blue colour was obtained, but the remaining two solutions became blue at once, and the blue compound was extracted by the ether on shaking. In the solution containing 2 cc. HNO_3, the colour in the ether layer in contact with the solution disappeared in about half an hour on standing; the colour was more brilliant and remained for a longer time in the experiment with 0·5 cc. HNO_3. The experiment was repeated with H_2SO_4 (1·20) instead of HNO_3: no colour was obtained with no acid or with 10 and 20 cc. of it; the most brilliant and most permanent colour was obtained in the experiment with 0·5 cc. acid. The experiment was repeated with 30 per cent acetic acid: in this case the best tests were obtained in the solutions containing 10 and 20 cc. of acid; with the more delicate solutions only a faint blue colour was obtained.

Another series of experiments was performed with solutions that contained 0·3 mgrm. Cr as K_2CrO_4, and 2 cc. HNO_3 (1·20) in about 20 cc.; 3 cc. ether and varying amounts of H_2O_2 (3 per cent) were added: with 10 cc. H_2O_2 no test was obtained, with 5 cc. a slight one, with 2 cc. a good test, but with 0·5 cc. H_2O_2 a much better one.

In all of these experiments in which the blue perchromic acid was formed, the blue colour disappeared completely in less than one hour. In some of them the solution was warmed to 50 or 60°: the blue colour disappeared very rapidly. These experiments prove that perchromic acid is a very unstable substance even in the absence of an excess of H^+ or of H_2O_2 and is still more so at higher temperatures.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, October 22nd, 1908.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

MESSRS. H. R. Lyell and C. T. Rutter were formally admitted Fellows of the Society.

The PRESIDENT referred to the loss sustained by the Society through the death, on August 25th, of Prof. A. H. Becquerel, who was elected an Honorary and Foreign Member in May, 1904; also of Sir Thomas Stevenson and Mr. Bennett H. Brough, who died on July 27th and October 3rd respectively.

On the question of admitting women to the Fellowship of the Chemical Society, the PRESIDENT announced that 1758 voting papers were received before the close of the ballot; of these there were, in favour of admission, 1094; against admission, 642; neutral, 22. The matter is now receiving the earnest attention of the Council.

The PRESIDENT further stated that he was authorised by the Council to inform the meeting that in all proceedings relating to the admission of women as Fellows, the Honorary Secretaries have throughout acted under the direction of the Council.

Certificates were read for the first time in favour of Messrs. Noel Charles Akers, 26, King's Avenue, Muswell Hill, N.; Maurice Barrett, Holly Bush, Headingley, Leeds; Robert Bickerstaffe, Chilterns, Wooburn Green, Bucks; William Sudderick Brakes, 137, Steade Road, Sheffield; Leonard Clement, B.A., Beamsley, Fairhaven, near Lytham; Robert Charles Cowley, College of Pharmacy and Chemistry, Brisbane; Hugh Cecil Duckworth, 66, Victoria Street, S.W.; Horace Barratt Dunnicliff, B.A., B.Sc., 39, Herne Hill, S.E.; Reginald Freeman Easton, 38, Edith Road, W. Kensington; Henry Fairburn, Northallerton; Arthur Frank Girvan, B.Sc., 8, Chatsworth Road, West Norwood, S.E.; John Henry Albert Hebron, B.Sc., 9, Buller Street, Derby; Grove Johnson, 124, Savoy Court, Strand, W.C.; Patrick Anderson Keiller, B.Sc., Colombo, Ceylon; Frank William Linch, 9, Gladstone Avenue, Manor Park, London, E.; Arthur Stanley Lindley, Prince Building, Medows Street, Bombay; Edward Pigott Minett, M.D., M.R.C.S., L.R.C.P., Guy's Hospital, S.E.; Cyril Lawrence Norman, 36, Halesworth Road, Lewisham, S.E.; Alexander Robert Normand, M.A., B.Sc., Wilson College, Bombay; Alexander Rennie, Johannesburg, Transvaal; Ezra Lobb Rhead, Stonycroft, Polygon Avenue, Levenshulme; Maurice Salamon, 64, Oxford Gardens, N. Kensington, W.; William Saunderson, B.Sc., The Armidale School, Armidale, N.S.W.; Ernest Sommerfeldt, Ph.D., The University, Tübingen; Francis George Henry Tate, Kilmersdon, Homecroft Road, Sydenham, S.E.; Robert Dickie Watt, M.A., B.Sc., P.O. Box 434, Pretoria, Transvaal; Arthur Weighell, Prince Building, Medows Street, Fort, Bombay; Frederick Williams, B.A., Bute Villa, Aberdare, South Wales; William George Winterson, B.Sc., 89, Salisbury Road, Barnet; Allister MacLean Wright, P.O. Box 617, Christchurch, New Zealand.

Of the following papers, those marked * were read :—

*199. "*The Relationship of Colour and Fluorescence to Constitution.* Part II. *Rhodamines of Mellitic Acid.*" By Oswald Silberrad and Charles Smart Roy.

Condensation products of mellitic acid with *m*-aminophenol and dimethyl-*m*-aminophenol were described.

The results confirm the conclusions arrived at in the previous paper by one of the authors (Silberrad, *Trans.*, 1906, lxxxix., 1788), in indicating that a quinonoid structure is not an essential integral part of intensely coloured and fluorescent compounds.

The work also appears to show that the lactone ring is much more stable in these compounds than in the less complex phthaleins already known. As in the case of resorcinol compounds (*loc. cit.*), the tetra-aminodixanthyl derivatives exist in two modifications, in which the xanthyl groups are in the meta- and para-positions with regard to one another respectively. The orientation of these groups was determined by the introduction of a third xanthyl group in the case of the meta-compounds.

As both these still contain carboxylic groups in the ortho-position with respect to one another, the formation of trixanthyl derivatives from the meta-compounds only affords an exceptionally good example of steric hindrance.

The following new compounds, together with their salts and derivatives, were described :—

Monoxanthyl derivatives. — 3 : 6-*Diamino*-9-*hydroxy*-*xanthylbenzene*-2-*carboxylactone*-3 : 4 : 5 : 6-*tetracarboxylic acid*. *Tetramethyl*-3 : 6-*diamino*-9-*hydroxyxanthylbenzene*-*pentacarboxylic acid* and its *pentaethyl* ester. *Tetraethyl*-3 : 6 - *diamino* - 9 - *hydroxyxanthylbenzenepentacarboxylic acid*.

Dixanthyl derivatives—*Octamethyl*-3 : 3′ : 6 : 6′-*tetra*-*amino*-9 : 9′-*dihydroxy* - m - *dixanthylbenzene*-2 : 4 : 5 : 6 - *tetracarboxylic acid* and its *ethyl* and *benzyl* esters. *Octaethyl*- 3 : 3′ : 6 : 6′- *tetra* - *amino*-9 : 9′-*dihydroxy* - p - *dixanthylbenzene*-2 : 3 : 5 : 6-*tetracarboxylic acid* and its *ethyl* ester. *Tetramethyl*-3 : 6-*diaminotetraethyl*-3′ : 6′-*diamino*-9 : 9′-*dihydroxy*-m-*dixanthylbenzene*-2 : 4 : 5 : 6 - *tetracarboxylic acid*. *Octaethyl*-3 : 3′ : 6 : 6′-*tetra*-*amino*-9 : 9′-*dihydroxy* - p-*dixanthylbenzene*-2 : 3 : 5 : 6-*tetracarboxylic acid*.

Trixanthyl derivatives. — *Hydrated dodecamethyl* - 3 : 3′ : 3″ : 6 : 6′ : 6″-*hexa* - *amino*-9 : 9′ : 9″- *trihydroxy*-s - *trixanthylbenzene* - 2 : 4 : 6 - *tricarboxylactone* and its *triethyl* ester.

Discussion.

Prof. Green expressed the opinion that, although the case was more complicated, the facts described by Dr. Silberrad were not greatly different from those which held for the simple rhodamines, and the evidence for or against a quinonoid constitution was of about the same character. The non-formation of a potassium salt was also true of the simple rhodamines, whilst the resistance to esterification might be attributed to steric hindrance, owing to the carboxylic groups being placed between xanthyl residues.

Dr. Silberrad, in reply, considered that the action of alkalis on the trixanthyl derivatives, and their insolubility even in concentrated potassium hydroxide, must be regarded as strong evidence in favour of the lactonic formula. The mono- and di-xanthyl compounds, which were shown to be inner salts, possessed the properties of strong tetra- and penta-basic acids respectively.

As to the observation that the rhodamines also formed potassium salts only with the utmost difficulty, it seemed to him that this should be regarded as evidence of their lactonic structure rather than as indicative that the trixanthyl derivatives of mellitic acid, which showed the same lactone-like property, possessed a quinonoid structure.

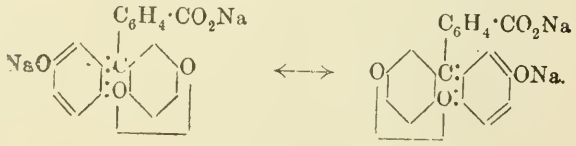
As to the possibility of steric hindrance being the explanation of the difficulty experienced in the esterification of the trixanthyl compounds, here again he thought that the evidence was in favour of the lactonic formula rather than the assumption of any such explanation, for if this were so, the formation of a tetraethyl ester from the meta-dixanthyl derivatives would offer more difficulty than the esterification of the para-compounds; experience showed, however, the converse to be the case, the meta-compound being the more readily esterified.

*200. "*Constitution of the Salts of the Phthaleins and the Cause of Colour in the Triphenylmethane Series.*" By Arthur George Green.

Whilst strong evidence has been adduced in favour of the quinonoid structure of the coloured salts and ethers of the phthaleins, there still remain several facts which are not fully explained. One of these is the remarkable difference in colour between the quinonoid diethyl ethers and the alkali salts (orange in the first case and violet-red in the second), whilst another is the circumstance that the substitution of one only of the phenolic hydroxyl groups by methoxyl, in either phenolphthalein or in quinolphthalein, suffices entirely to prevent the formation of coloured salts with alkalis.

By an extension of von Baeyer's theory of oscillatory quinonoid bonds, employing the usual Fittig formula for quinonoid compounds instead of the Graebe formula used by von Baeyer, and by the assumption that the movement of the metallic or acid ion between the two salt-forming groups is the determining cause of the quinonoid oscillation, a satisfactory explanation can be given of the above and other facts, such as the effect of salt formation on colour intensity, the function of auxochromic groups, and the increase of basicity according to the "power law." An explanation is also afforded of the observation that the behaviour of dimethylanilinephthalein, the basic analogue of phenolphthalein, towards acids is analogous to that of the latter towards alkalis, these compounds giving under specific conditions a deep violet colour readily destroyed by an excess of the reagent.

In the quinolphthalein series, the possibility of a meta-quinonoid structure for the coloured alkali salts as suggested by R. Meyer was discussed in relation to the recent work of Green and King. The conclusion was drawn that the facts are best explained by the assumption of an ortho-quinonoid linking oscillating between the two benzene nuclei :—



Discussion.

Dr. Silberrad suggested that it would be a fuller and more complete explanation of the experimental evidence if colour were wholly attributed to some inner molecular oscillation, such as that so well illustrated by the examples considered by Prof. Green, and not to the presence of a quinonoid group at all; thus the ethers of these compounds were almost colourless, yet they still contained the same quinonoid constitution, and differed from the parent compound only in that they could not exhibit inner molecular oscillation.

He agreed that the presence or absence of a quinone group exercised considerable influence on the colour of any compound, but so would any other considerable constitutional change.

Further, he thought that the wide application of the quinonoid configuration to coloured compounds by analogy was open to criticism. Prof. Green's observation, that the coloured salts of the rhodamines become colourless in the presence of an excess of acid, did not apply to their mellitic analogues, which yielded coloured solutions with any excess of acid.

Dr. Morgan remarked that R. Meyer and Desamari's recent demonstration of the existence of tribromo-*m*-benzo-quinone,—

afforded important experimental evidence in favour of the view that certain phthaleins might have a meta-quinonoid structure.

In connexion with the theory that the colour of triphenylmethane dyes was associated with an oscillation of the quinonoid phase, it was noteworthy that diphenylnaphthylmethane dyes could be obtained from naphthastyril, a peri- or 1 ; 8-derivative of naphthalene, because, owing to the configuration of the 1 : 8-naphthylene residue present in these colouring matters, it was difficult to see how this oscillation would take place.

*201. "*The Relation between Absorption Spectra and Chemical Constitution.* Part X. *Unsaturated Acids of the Benzene Series.*" By EDWARD CHARLES CYRIL BALY and KONRAD SCHAEFER.

The absorption spectra of cinnamylideneacetic, cinnamylidenemalonic, benzylidenemalonic, and cinnamic acids have been examined with a view to determining the influence of substitution of the acidic hydrogen atoms by metals and alkyl groups. In the case of cinnamylideneacetone, $C_6H_5{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}C(=O){\cdot}CH_3$, a strongly marked absorption band is developed, owing to the isorropesis arising from the conjugation of the carbonyl group with the two double linkings and the phenyl group. In cinnamylideneacetic acid, where the methyl group is replaced by hydroxyl, the absorption band is shifted towards the violet, owing to the fact that the free residual affinity of the carbonyl group is decreased by the juxtaposition of the hydroxyl group. This decrease of free residual affinity is most marked in the case of the readily ionised sodium salt, and least marked with the acid when the ionisation is restrained by the addition of hydrogen chloride. This effect has been observed in the four acids mentioned, and is especially marked in the case of cinnamylidenemalonic acid. The addition of alkali to this acid causes a shift of the absorption band from just outside the visible region to just beyond it, so that the free acid appears to be coloured yellow, and its sodium salt appears to be colourless. The results throw some light on the catalytic action of mineral acids on the esterification process.

*202. "*Relation between Chemical Constitution and Physiological Action in certain Substituted Aminoalkyl Esters.*" By FRANK LEE PYMAN.

Several substituted aminoalkyl esters have been prepared with the object of producing a cocaine substitute ; none of these, however, are suitable for the purpose, since such as possess anæsthetic properties are also toxic and irritant. These substances were prepared by benzoylating (in two cases, phthaloylating) the corresponding amino-alcohols, two of which 1 : 4-*diethanolpiperazine* (m. p. 134—135°) and *β-hydroxy-β-3 : 4-methylenedioxyphenylethyldimethylamine*, have not previously been described. (Where melting-points are not given, the free base did not crystallise). The chemical, physical, and physiological properties of the following aminoalkyl esters and their salts have been examined : — *Dibenzoyloxymethyldiethylamine*, *dibenzoyloxytriethylamine*, *βγ-dibenzoyloxydimethylpropylamine*, *βγ-dibenzoyloxydiethylpropylamine*, *βγ-dibenzoyloxypiperidylpropane* (m. p. 64—65°), *piperidylethyl benzoate*, *s-di-β-benzoyloxy-1 : 4-diethylpiperazine* (m. p. 104—105°), *diethylaminoethyl phthalate*, *piperidylethyl phthalate*, *β-benzoyloxy-β-3 : 4-methylenedioxyphenylethyldimethylamine*.

203. "*The Passage of Hydrogen through a Palladium Septum, and the Pressure which it Produces.*" By DEMETRIUS TSAKALOTOS.

It was shown by Sir William Ramsay (*Phil. Mag.*, 1894, [5], xxxviii., 206) that hydrogen when it passes through the walls of a palladium tube filled with a gas (N_2, CO, CO_2, CN) at atmospheric pressure, raises the pressure in the tube by nearly one atmosphere when the external pressure of the hydrogen is one atmosphere. There is always a small deficit in pressure, however, for the rise in pressure produced by the entry of the hydrogen never attains that of the atmosphere. The amount of this deficit depends on the nature of the gas originally in the tube.

The experiments to be recorded were made with the object of ascertaining whether, if the tube were initially filled with an indifferent gas, the final pressure would be the theoretical one. Argon was chosen for this purpose. The method employed differed little from that described by Ramsay. The tube was filled with pure dry argon at atmospheric pressure, and at a temperature of 280° (boiling-point of bromonaphthalene) ; it was then exposed on its external surface to an atmosphere of hydrogen, carefully purified and dried. If p be the external pressure of the hydrogen, and p' the internal pressure, that is, the pressure due to the hydrogen after the gas had ceased to enter, the results of the experiments are as follow :—

	I.	II.	III.	Theory.
p'/p . .	0·9281	0·9189	0·9242	1·000

The mean mean result is 0·9238.

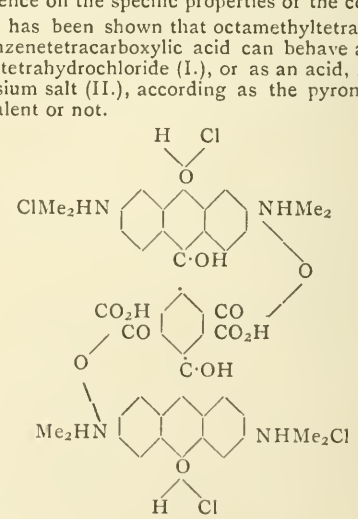
This result does not appreciably differ from that previously obtained by Ramsay ; the figures varied between 0·8984 and 0·9693.

204. "*Constitution of the Phthaleins of Mellitic and Pyromellitic Acids.*" By OSWALD SILBERRAD.

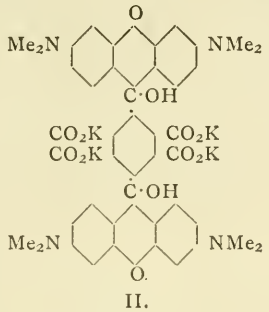
In a previous paper, the author described (*Trans.*, 1906, lxxxix., 1789) condensation products of mellitic and pyromellitic acids with resorcinol to which were assigned carbinol formulæ, as being the most in accord with observed facts. Subsequently, quinonoid formulæ have been suggested (compare, Green, *Proc.*, 1907, xxiii., 12).

In considering the possibility of so formulating these compounds, it should not be lost sight of that the necessity for attributing quadrivalency to the pyrone oxygen atom is hardly in accord with the properties of the compounds in question ; they show none of the basic properties generally attributed to this element when so linked ; on the contrary, they form salts up to the full basicity of the acid groups present. Further, recent work by the author has shown that when present in analogous compounds a quadrivalent oxygen atom impresses a strongly basic influence on the specific properties of the compound.

Thus it has been shown that octamethyltetra-aminodixanthylbenzenetetracarboxylic acid can behave as a base, forming a tetrahydrochloride (I.), or as an acid, forming a tetrapotassium salt (II.), according as the pyrone oxygen is quadrivalent or not.



I.



II.

205. "*A New Form of Gas Burette.*" By ARTHUR EDWIN HILL.

A novel form of gas burette was described which consists of a series of ten bulbs, each with a capacity of 10 cc., connected by short, narrow, graduated tubes. Fractional parts of 10 cc. are measured in a narrow side tube, which has a capacity of 10 cc. graduated into twentieths of a cc.; this is connected to the main vessel by a capillary tube, and forms one arm of a U-shaped manometer, which indicates the pressure of the gas inside the burette. The apparatus is provided with a capillary tap at each end, and is connected by flexible rubber tube with a levelling reservoir.

206. "*A Molecular Compound of Trinitroacetylaminophenol and β-Naphthol.*" By RAPHAEL MELDOLA and JAMES GORDON HAY.

The 2 : 3 : 5-trinitro-4-acetylaminophenol described by one of the authors in a former paper (*Trans.*, 1906, lxxxix., 1935) combines readily with β-naphthol when solutions containing equimolecular weights of the two compounds are mixed together and boiled for a few minutes. Acetic acid or alcohol can be used as a solvent. If the solution is not too dilute, the molecular compound separates out on cooling in dense red prisms, melting with decomposition at 184—185° :—

0·1196 gave 0·2216 CO_2 and 0·0392 H_2O. C = 50·33; H = 3·6.

0·0895 gave 9·9 cc. N_2 (moist) at 14·5° and 755·8 mm. N = 12·89.

0·1245 gave 13·5 cc. N_2 (moist) at 10° and 752·3 mm. N = 12·85.

$C_8H_6O_8N_4,C_{10}H_8O$ requires C = 50·2; H = 3·23; N = 13·02 per cent.

That the compound is "molecular" is shown by its behaviour towards reagents. By alkali alone it is dissolved with an orange colour, which gradually disappears on standing, and, on acidifying, the solution yields only the products of decomposition of trinitroacetylaminophenol and β-naphthol. With alkali and dimethyl sulphate, the compound gives β-naphthyl methyl ether and the products of decomposition of the trinitroacetylaminophenol. By continued crystallisation from acetic acid, the compound is gradually resolved into its components.

The formation of this molecular compound is of interest as, so far, β-naphthol is the only phenol which has been found to enter into combination with the trinitro-compound. The latter, unlike picric acid and other polynitro-compounds, does not appear to form molecular compounds with hydrocarbons, This point is, however, still undergoing investigation, and the authors communicate this note as a preliminary statement of the results of their experiments.

207. "*The Products of Reduction of Azoxybenzene.*" (Preliminary Note). By LESLIE HAMILTON BERRY.

The author is unable to confirm the statement of Schmidt and Schultz (*Ber.*, 1879, xii., 484), that stannous chloride and hydrochloric acid reduce azoxybenzene to aniline, very little benzidine being formed.

He finds, on the contrary, that in no case is the yield of aniline more than 35 per cent, and the principal product is benzidine.

208. "*The Chlorination of Para-nitroaniline.*" By BERNARD FLÜRSCHEIM.

Hitherto no satisfactory method for introducing two atoms of chlorine into *p*-nitroaniline has been known. More especially by the action of chlorine gas much resinous matter was formed. The author finds, however, that a quantitative yield of pure dichloro-*p*-nitroaniline is obtained when *p*-nitroaniline is chlorinated in a mixture of acetic and mineral acids at a low temperature; this result is in accordance with theoretical deduction.

209. "*Syntheses with the Aid of Monochloromethyl Ether.* Part I. *The Action of Monochloromethyl Ether on the Sodium Derivatives of Ethyl Malonate and Ethyl* Iso*propylmalonate.*" By JOHN LIONEL SIMONSEN.

Monochloromethyl ether and ethyl sodiomalonate readily condense with the formation of *ethyl β-methoxymethylmalonate* :—

$$MeO{\cdot}CH_2Cl + CHNa(CO_2Et)_2 \rightarrow MeO{\cdot}CH_2{\cdot}CH(CO_2Et)_2;$$

this is a colourless oil, which boils at 121—122°/15 mm. When hydrolysed with hydrochloric acid, it is converted into *cis-cyclo*butane-1 : 3-dicarboxylic acid. Other derivatives of ethyl β-methoxymethylmalonate have also been prepared.

When monochloromethyl ether and ethyl *iso*propylsodiomalonate are condensed, *ethyl β-methoxymethyliso*propylmalonate is formed :—

$$MeO{\cdot}CH_2Cl + CNa(CHMe_2)(CO_2Et)_2 \rightarrow MeO{\cdot}CH_2{\cdot}C(CHMe_2)(CO_2Et)_2.$$

This substance boils at 130°—132°/20 mm., and on hydrolysis yields *β-methoxymethyliso*propylmalonic acid, which crystallises in plates melting at 83—84°.

210. "*The Effect of Constitution on the Rotatory Power of Optically Active Nitrogen Compounds.* (Part III.). By REGINALD WILLIAM EVERATT and HUMPHREY OWEN JONES.

An account was given of the resolution of *p*-tolylbenzylmethylallylammonium hydrogen tartrate. The corresponding iodide has been prepared by Wedekind (1903), who found that the camphorsulphonate could not be resolved. This compound is of interest, since it contains two groups, benzyl and tolyl, which have the same mass. The salt of the lævorotatory base was isolated by crystallising about thirteen times from alcohol and ether.

The molecular rotatory power of the ion at 15° is − 246°, that of the iodide in alcohol is − 257°, and in chloroform is − 267°.

The rotatory power of the ion is greater than that of the ion of the corresponding phenyl (167°) or *p*-bromophenyl compound (191°). This is not in agreement with the requirements of Guye's hypothesis as applied to the case of nitrogen, and shows that the constitution of a group may exert such a marked effect on the rotatory power of a compound as to veil completely the effect of mass.

211. "*Studies on the Cobaltinitrites.*" By MARY CUNNINGHAM and FREDERICK MOLLWO PERKIN.

On adding a solution of a salt of a primary amine to a strong solution of sodium cobaltinitrite, a yellow or orange precipitate is produced, which is frequently crystalline. If the solution is not kept cold, the product is apt to decompose. Analysis shows that three molecules of the amine combine with the cobaltinitrite residue. Thus the compound obtained from methylamine has the formula $(CH_3{\cdot}NH_3)_3Co(NO_2)_6$. The authors have prepared the methylamine, ethylamine, aniline, *m*- and *p*-bromoaniline, and the *p* toluidine compounds, all of which have been analysed. It is found that, unless carefully dried as soon as prepared, the compounds are extremely unstable, and even then it is necessary to analyse them very soon after preparation. Diethylamine also forms a crystalline compound, $[(C_2H_5)_2NH_2]_3Co(NO_2)_6$, which is fairly stable. The methylaniline compound decomposes before it can be

dried, and apparently a nitroso-compound is produced. From dimethylaniline, the *p*-nitroso-derivative is at once formed.

212. "*The Relation between Viscosity and Chemical Constitution.* Part II. *The Existence of Racemic Compounds in the Liquid State.*" By ALBERT ERNEST DUNSTAN and FERDINAND BERNARD THOLE.

The authors have applied the viscosimetric method to the above problem, and have determined the viscosities at 25° of the active and inactive forms of tartaric acid, malic acid, pinene, camphene, and limonene.

They find that, in general, the inactive form has the lower viscosity, and argue that this points to the existence as such of the racemic compound in the liquid state.

They have further examined the viscosity of solutions of sodium ammonium tartrate at different temperatures, and find that a change of curvature appears at 28·7°; hence a new method of determining transition points is to be added to those already in vogue.

213. "*The Formation of Polyiodides in Nitrobenzene Solution.* Part IV. *The Electrolytic Dissociation of the Polyiodides of the Alkali Metals and Ammonium Radicles.*" By HARRY MEDFORTH DAWSON and COLIN GYRTH JACKSON.

The authors have investigated the electrolytic dissociation of the polyiodides in nitrobenzene solution by means of freezing-point and electrical conductivity measurements. The data obtained show that the polyiodides are ionised to a considerable extent.

In the case of the polyiodides of potassium, for which several series of freezing-point measurements were made, the depressions, calculated from the chemical dissociation on the assumption that the higher polyiodides are ionised to the same extent as the tri-iodide, are in good agreement with the observed values. It is probable that the penta-, hepta-, and ennea-iodide of each alkali metal and ammonium base are equally ionised, although the degree of ionisation appears to vary with the nature of the cation. On the other hand, evidence has been obtained that, in some cases, the tri-iodides are not ionised to the same extent as the higher polyiodides.

As the result of comparative measurements of the conductivity of solutions of the iodides and tri-iodides it is found that the tri-iodides are electrolytically dissociated to a much greater extent than the iodides. In the case of tetrapropylammonium iodide, for which, on account of its solubility in nitrobenzene, a comparison by the freezing-point method has been possible, the conclusions drawn from the conductivity data are completely confirmed.

The mobilities of the polyiodide ions have been deduced by combining the results of transport measurements with the freezing-point and conductivity data.

Finally, determinations of the molecular solution-volume of iodine and the polyiodides have been made. The results show that the volume of combined iodine differs from that of iodine in the free condition.

214. "*The Direct Action of Radium on Copper and Gold.*" By EDGAR PHILIP PERMAN.

The direct action of the radiations from a radium salt on a pure copper salt has been investigated; the salts were placed in small capsules facing one another in a wide tube, which was exhausted and sealed.

In the case of gold, the two salts were left in solution together, and in another experiment, gold and radium barium sulphate were precipitated together, thoroughly washed, and allowed to stand.

After four months, no trace of lithium could be detected by spectroscopic examination, and the conclusion is drawn that if any copper or gold is converted into lithium, it cannot be more than the one hundred-millionth part of the weight of the radium salt per day in the case of copper, and the one two-hundred-millionth part in the case of gold, under the conditions of the respective experiments.

215. "*The Atomic Volumes of Phosphorus.* Part II. *Phosphorus and Bromine.*" By EDMUND BRYDGES RUDHALL PRIDEAUX.

The specific volumes of liquid phosphorus pentabromide and the pressures of its saturated vapour at various temperatures have been measured. From the values of the vapour pressures from 20° to 100°, and of the coefficients of expansion and molecular volumes from 85° to 100° and 100° to 165°, the true boiling-point is placed at 106°, and the molecular volume at this temperature is 157·3. A review of the molecular volumes of the chlorides, bromides, phosphoryl chloride, and phosphoryl dichlorobromide shows that the atomic volumes of tervalent are greater than those of quinquivalent phosphorus.

216. "*Isomeric Chromous Chlorides.*" By ELIZABETH MARY RICH.

The author has devised a rapid and convenient method of preparing pure chromous chloride, which is thus rendered practically available for use in all kinds of gas analysis. Two isomeric series of hydrates and their solutions have been studied. The green isomeride has the formula $CrCl_2,4H_2O$, identical with the blue salt. Its green solution contains the ions $CrCl^{\cdot}$ and Cl'.

217. "*The Relative Atomic Weights of Hydrogen and Chlorine.*" By ROBERT WHYTELAW GRAY and FRANK PLAYFAIR BURT.

The ratio H : Cl has been measured by a method which is different from that employed by Dixon and Edgar (*Phil. Trans.*, 1905, ccv., 169), or by Noyes and Weber (*Journ. Am. Chem. Soc.*, 1908, xxx., 13). The investigation was carried out with hydrogen chloride obtained from several sources, and purified by fractional distillation. (1). The density of the gas was determined, the gas being condensed on charcoal and weighed. The mean of twenty experiments gave for the weight of a normal litre of gas the value 1·63900 ± 0·00004 grms., or making a small correction for the amount of gas condensed on the surface of the walls of the density bulb and absorbed by the tap grease, 1·63885 grms. (2). The gas was analysed volumetrically by passage over heated aluminium. By this means the volume of hydrogen contained in exactly two volumes of hydrogen chloride measured at 0° and 760 mm. was determined, and this gave the exact ratio of the volumes of hydrogen and hydrogen chloride which under standard conditions contain the same number of molecules.

Eight measurements with gas from different sources gave for the volume ratio $H_2 : HCl$ the mean value 1·00790 ± 0·00002.

From these two results, the molecular weight of hydrogen chloride may be directly calculated as follows :—

If D_{HCl} represents the measured weight of a litre of hydrogen chloride at 0° and 760 mm., lat. 45°, and D_{H_2} represents the known weight of a litre of hydrogen at 0° and 760 mm., lat. 45°, and if—

$$\frac{V_{H_2}}{V_{HCl}}$$

expresses the ratio of the volumes of hydrogen and hydrogen chloride, which at 0° and 760 mm. contain the same number of molecules; then the molecular weight of hydrogen chloride is given by the expression—

$$\left(\frac{D_{HCl}}{D_{H_2}} \times \frac{V_{HCl}}{V_{H_2}}\right) \times 2.$$

On the basis of Morley's values for the normal density of hydrogen, namely, 0·089873 grm. per litre, and for the atomic weight of hydrogen, namely, 1·00762, the molecular weight of hydrogen chloride is—

$$\left(\frac{1·63885}{0·089873} \times \frac{2}{1·00790}\right) 1·00762 = 36·461,$$

and the atomic weight of chlorine = 35·453. This agrees almost exactly with the results of Noyes and Weber, namely, Cl = 35·452, but is 1/3500 part lower than Dixon and Edgar's number, namely, 35·462.

218. "*The Interaction of Hydrogen Dioxide and Sulphides.*" By MAUD GAZDAR and SAMUEL SMILES.

The usual method of preparing sulphoxides from sul-

phides by means of concentrated nitric acid is useless when applied to sensitive compounds, such as di-*p*-aminophenyl sulphide or thiodiglycollic acid. Hydrogen dioxide in acetone or aqueous solution reacts at the ordinary temperature with the sulphides, giving almost quantitative yields of the corresponding sulphoxide. The reaction can be applied to sulphides of very varied character, for, besides amyl, benzyl, and phenetyl sulphoxides, the hitherto unknown *di-p-aminophenyl sulphoxide* and *thionyldiglycollic acid* were obtained. Diphenylene disulphide and tetranitrodiphenyl disulphide are not attacked by the reagent under ordinary conditions.

219. "*The Influence of Solvents on the Rotation of Optically Active Compounds.* Part XIII. *Ethyl Tartrate in Aromatic Nitro-derivatives. Influence of Temperature change on Rotation in Solution.*" By Thomas Stewart Patterson.

The influence of the aromatic nitro-derivatives as solvents on the rotation of ethyl tartrate was described. The effect of temperature-change on the rotation of these and other solutions was also discussed.

220. "*The Isomeric Menthols.*" (Preliminary Note). By Robert Howson Pickard and William Oswald Littlebury.

According to theory there should be eight optically active forms of 1-methyl-4-*iso*propyl*cyclo*hexan-3-ol corresponding in pairs with four racemic compounds. Of these menthols, one, the ordinary *l*-menthol, occurs in nature, whilst the existence of others has been indicated by the researches of Beckmann, Kondakoff, and Brunel. It is now found that these compounds can be separated by the fractional crystallisation of suitable esters, such as the hydrogen phthalates, hydrogen succinates, &c.

By the reduction of thymol with hydrogen in the presence of reduced nickel, Brunel (*Comptes Rendus*, 1905, cxl., 252) obtained a low-melting thymomenthol, which he considered was transformed into an isomeride by conversion into an ester and subsequent hydrolysis. The authors have been able to show that this "α" thymomenthol of Brunel contains three (or perhaps all four) of the racemic compounds mentioned above. Up to the present, two of these have been fully characterised and resolved into their optically active components by fractional crystallisation of various alkaloidal salts of some of their acid esters (compare Pickard and Littlebury, *Trans.*, 1907, xci., 1974).

The first of these racemic menthols melts at 25°, and forms a *hydrogen succinate*, m. p. 86°, and also a *hydrogen phthalate*, m. p. 131°, the latter of which by fractional crystallisation of either its cinchonine or brucine salt yields a lævorotatory isomeride. When hydrolysed, this lævoester yields a menthol identical in melting-point and rotation with the natural menthol.

The second of the racemates melts at 48—50°, and forms a *hydrogen phthalate*, m. p. 175—177°, which is readily resolved into its active components by crystallisation of the brucine salt.

SOCIETY OF CHEMICAL INDUSTRY.
(London Section).

Ordinary Meeting, November 2nd, 1908.

Dr. Lewkowitsch in the Chair.

A Paper entitled "*Chemical Industry in relation to Agriculture*," by Prof. Adolf Frank (Charlottenburg), was read by the Chairman.

After referring to the great services of Liebig to agriculture, the author gave an historical survey of the manufacture and agricultural uses of phosphates and the production of potash. Ammonium sulphate, Chile saltpetre, and the utilisation of atmospheric nitrogen were also discussed, and an account was given of the author's own work in effecting the combination of atmospheric nitrogen with carbides of the alkalis and the alkaline earths. By decomposing the calcium cyanamide with water under high pressure ammonium salts are formed. Possibilities of calcium cyanamide as a fertiliser are dealt with, and some statistics relating to the output of calcium carbide are included. The work of Mond on the simultaneous production of power gas has made it possible to utilise the large stores of energy accumulated in bog areas in the form of peat. The author and Caro, with the assistance of Mond, have been able without difficulty to gasify peat containing 50 to 55 per cent of water.

NOTICES OF BOOKS.

Dyeing and Cleaning. By Frank J. Farrell, M.Sc. (Vict.). London: Charles Griffin and Co., Ltd. 1908.

This book contains complete accounts of the general principles of the usual methods of dry and wet cleaning, and includes a chapter on dyeing which is written specially from the point of view of the job dyer, so that the problems which he has to face are treated at greater length than would be necessary for a manual on the dyeing of piece goods. The book is thoroughly practical, and will be a useful handbook for dyers and cleaners. A short chapter on technology gives brief accounts of the origin of the different animal and vegetable fibres, and the action of acids and alkalis upon them is described in some detail. Dry cleaning by various processes is next discussed, the treatment of the articles to be cleaned being described from the moment they are received and marked, while a chapter at the end of the book explains methods of finishing, which are of more importance for wet-cleaned and dyed than for dry-cleaned articles. Wet cleaning and dyeing are treated in outline, though no doubt fully enough for the purpose for which the book is intended, and special methods which have to be applied to skins, furs, feathers, &c., are given some consideration.

From the Interim Report issued by the Departmental Committee on Dangerous Trades the sections relating to dry cleaning are reprinted.

A defect of the work, which is not uncommon in this kind of book, is the reproduction of pictures of various types of machines. These often occupy the whole page, except perhaps for a few lines top and bottom; they are of no particular use to the practical man, who is probably already well acquainted with the machines, nor to the beginner, who learns far more from the examination of one or two models, and who moreover would want to study sections more than photographs of exteriors; thus they add to the bulk of the book without increasing its value in the same proportion.

The Extra Pharmacopœia of Martindale and Westcott. Revised by W. Harrison Martindale, Ph.D., F.C.S., and W. Wynn Westcott, M.B.Lond., D.P.H. Thirteenth Edition. London: H. K. Lewis. 1908.

The thirteenth edition of the Extra Pharmacopœia contains information relating to many new remedies and fresh preparations which have recently come into use, and the developments of various branches of pharmacy are summarised. The valuable work which has been done during the last few years on vaccines and antitoxins is reviewed, and several new vaccines are described. The section on radiology has been brought up to date, and many parts of the analytical section have been reprinted; for the first time a list of the results of the analysis of various patent medicines is included. In spite of the fact that the new edition contains much more material than the old, the book is less thick than before, owing to the use of smaller type and thinner paper.

House Painting. By ALVAH HORTON SABIN, M.S. New York: John Wiley and Sons. London: Chapman and Hall, Limited. 1908.

THE householder who likes to have some idea of what he is paying for when he has his house painted may refer to this book for practical information on suitable pigments, methods of applying paints, &c. The painter will probably find nothing in it that he did not know before, though it contains many counsels of perfection which he finds it convenient to forget. Glazing and papering are included, and copious directions are given to help the amateur to do his own papering and decorating.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

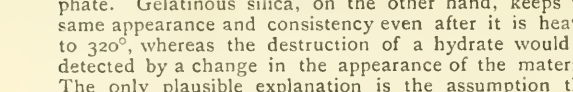
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvii., No. 16, October 19, 1908.

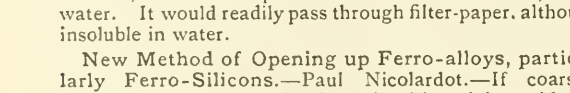
Precipitated Silica.—Henry Le Chatelier.—Silica loses all its water at 100° under atmospheric pressure, or in a vacuum at the ordinary temperature. Hence its hydrates, if they exist, are not stable. It is known that a hydrate at temperatures at which it is stable has a tension of efflorescence lower than the vapour tension of pure water, but this vapour tension increases more rapidly than that of water, and at a certain temperature, which is generally lower the less stable the hydrate is, the substance and water have exactly the same vapour tension. Above this temperature the hydrate is not stable. The temperature is 32° for sodium sulphate and 150° for calcium sulphate. Gelatinous silica, on the other hand, keeps the same appearance and consistency even after it is heated to 320°, whereas the destruction of a hydrate would be detected by a change in the appearance of the material. The only plausible explanation is the assumption that silica does not form hydrates, but always exists in the anhydrous state. Precipitated silica is in a state of fine division, and forms pastes of variable consistency with water. It would readily pass through filter-paper, although insoluble in water.

New Method of Opening up Ferro-alloys, particularly Ferro-Silicons.—Paul Nicolardot.—If coarsely powdered ferro-silicon is heated with sulphur chloride bubbles of gas are evolved at 70°; the action becomes violent at 100°, but then white fumes are evolved, indicating the formation of silicon chloride. With ferro-chromium the action does not begin till a temperature above 120° is reached, while with ferro-titanium it begins at 70°. If the vessel in which the reaction takes place is fitted with a cork through which the tube of a reflux condenser passes, all the chlorides can be retained, and thus the refractory alloys are completely opened up. The same method can be employed for analytical purposes for ferro-titaniums and ferro-silicons, the titanic oxide and silicon being weighed.

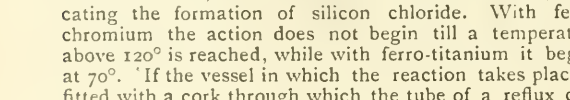
Migration of Naphthyl Group in Iodohydrins of the Naphthalene Series.—MM. Tiffeneau and Daudel.—The tendency of the aromatic radicle to migrate under the action of I + HgC is shown by the scheme—



In the naphthalene derivatives, *e.g.*, the allyl, isoallyl, pseudoallyl, and vinyl compounds the phenyl migration takes place in exactly the same way, the reaction being—



By analogy from the reaction with styrolene it must be assumed that the reaction with naphthylethylene is accompanied by the migration of a naphthyl group—



Modification of the Method of Preparing Monomethylamine by Brominated Acetamide.—Maurice François.—The brominated solution is prepared by dissolving acetamide in bromine, adding water and calcium carbonate, and filtering the liquid. Thus a clear red liquid is obtained It is added to cold caustic soda solution and the white turbid liquid is heated in a special tube to 100°; the raw product is distilled in a current of steam and the monomethylamine can then be converted into chlorhydrate by the action of hydrochloric acid. The yield is 72 per cent of the theoretical yield.

State of Colouring Matters in Solution.—L. Pelet-Jolivet and A. Wild.—The authors have studied different coloured solutions, *e.g.*, fuchsine, methylene blue, &c., by the method of conductivity and with the aid of the ultramicroscope, and find that the colouring matter exists in the dissociated state, or in some cases in the colloidal state. The addition of electrolytes by the action of ions of opposite signs favours the passage of the coloured solution into the state of a false solution. Colouring matters in solution and dissociated form ions of unequal dimensions; the inorganic ion Cl, K, Na, &c., is always relatively smaller than the organic ion.

MISCELLANEOUS.

Royal Institution.—The eighty-third Christmas course of juvenile lectures, founded at the Royal Institution in 1826 by Michael Faraday, will be delivered this year by Prof. William Stirling, M.D., LL.D., D.Sc., his subject being "The Wheel of Life." The course, which will be fully illustrated, commences on Tuesday, December 29, at 3 o'clock, and will be continued on December 31, 1908, January 2, 5, 7, and 9, 1909.

Chemical Society Research Fund.—A meeting of the Research Fund Committee will be held in December next. Applications for grants, to be made on forms which can be obtained from the Assistant Secretary, must be received on or before Monday, December 7, 1908. All persons who received grants in December, 1907, or in December of any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be in the hands of the Hon. Secretaries not later than Tuesday, December 1. The Council wish to draw special attention to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is to be more or less especially devoted to the encouragement of research in Inorganic and Metallurgical Chemistry. Furthermore, that the income due to the sum accruing from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the Coal-tar and Allied Industries.

MEETINGS FOR THE WEEK.

MONDAY, 23rd.—Royal Society of Arts, 8. (Cantor Lecture). "Twenty Years Progress in Explosives," by O. Guttmann.

WEDNESDAY, 25th.—Royal Society of Arts, 8. "The Goldfields of Eastern Peru and Bolivia," by Sir W. Martin Conway.

BIRMINGHAM MUNICIPAL TECHNICAL SCHOOL.

Applications are invited for the Post of DEMONSTRATOR AND JUNIOR LECTURER in the METALLURGICAL DEPARTMENT. Commencing salary £125. The last date for sending in applications is DECEMBER 7, 1908.

Full particulars of the Post will be sent on application to

GEO. MELLOR, Secretary.

Offices of the School, Suffolk Street,
November 16, 1908.

THE CHEMICAL NEWS.

Vol. XCVIII., No. 2557.

THE PRESENT STATE OF OUR KNOWLEDGE OF RADIO-ACTIVITY.*

By A. DEBIERNE.

(Concluded from p. 248).

V.

The following is the principal fact which has led to these theories :—In different circumstances it is possible to produce, by the aid of radio-active substances of constant and permanent activity, phenomena of radio-activity the intensity of which decreases with time.

Pierre Curie and Mdme. Curie first observed this new property in the salts of radium. They placed in the same receptacle different objects and a certain quantity of a product containing radium ; they proved that the objects, after having been thus left beside radium salt, themselves became radio-active ; they spontaneously emitted a radiation perfectly analogous to that of radium, producing the ionisation of the air, phosphorescence, and photographic action. These radio-active phenomena disappear fairly quickly with time, after the action of the radium has been stopped. Pierre Curie and Mdme. Curie called them induced radio-activity.

A short time afterwards Rutherford observed the same phenomenon with thorium salts. He proved, moreover, that gases which have passed over thorium oxide possess a radio-activity which rapidly decays with the time. He at once conjectured that the gases contain a special radio-active gaseous substance, to which he gave the name thorium emanation.

I observed the same phenomena with actinium salts. Later, I noticed that the temporary phenomena of radio-activity could be obtained by carrying out certain chemical separations. Thus, if a barium salt is added to a solution of an actinium salt and the two metals are then separated by the action of ammonia, it is found that the barium salt acquires a fairly strong activity which disappears with time. As we shall see later, the presence of the barium has no influence upon the production of the phenomenon.

The phenomenon of induced radio-activity was studied by Pierre Curie and various collaborators. It was shown that the immediate cause of the phenomenon is in the gas which has been in contact with the radium salt; the gas is itself radio-active, and also contains an emanation which disappears with time. The laws of the decrease of the intensity of the different phenomena were also studied in detail. The presence of an emanation was proved in the case of actinium as well.

A general theory which linked up all these phenomena was put forward by Rutherford and Soddy, after a series of experiments carried out with thorium. They first proved that it is possible to obtain with the compounds of thorium a phenomenon analogous to that which I had discovered with actinium ; *i.e.*, temporarily radio-active substances could be extracted by the aid of chemical separations. They studied the laws of the phenomenon, and they interpreted it as follows :—They supposed that the existence of radio-active phenomena, whether these phenomena appear to be permanent or temporary, is connected with the presence of special radio-active substances, and that the disappearance or appearance of the phenomena of radio-activity indicates the destruction or formation of these active substances. Thus this is an extension of the views which led to the discovery of radium.

They named these new active substances in different ways. Thus, the hypothetical substance which can be separated chemically from thorium, and the activity of which disappears gradually with time, they called thorium X. They showed that thorium X is produced continuously by thorium, and that its activity is an important part of the activity of thorium salts ; it is the thorium X which produces the thorium emanation, and the emanation produces the induced activity. This induced activity, detected in substances which have been in contact with the emanation, is attributed to the deposit of new active substances, which have been called thorium A and thorium B.

Now, the researches of Pierre Curie on the disappearance of the activity excited by radium salts showed that the existence of several different kinds of radio-activity following on one another must be admitted. According to the above theory this shows the presence of several active substances derived from radium emanation ; these have been called radium A, radium B, and radium C. The laws of the phenomenon also show that the formation of one term of a series is proportional to the destruction of the preceding term ; for instance, the formation of radium C is proportional to the destruction of radium B, which is most simply explained by supposing that radium B is destroyed to form radium C.

Researches on actinium have also shown a succession of different substances, actinium X, emanation, actinium A, actinium B.

In fact, these laws of the formation and destruction of active substances are exactly the same as those observed with ordinary chemical reactions in the case of monomolecular transformations. When a substance A undergoes a monomolecular transformation the quantity which is transformed in a given time is proportional at each instant to the quantity still in existence, $dq - Kqdt$. K is the coefficient of velocity of the transformation. The law of decay is thus a simple exponential law ; it has been verified in a certain number of cases, in particular in the case of the transformation of acetochloranilide into *p*-chloracetanilide. The verification is generally very difficult to obtain in the case of ordinary chemical actions, for the determinations are often almost impossible. In the case of the radio-active transformations, on the contrary, it is possible to obtain a perfect verification by measurements of the radio-activity.

If a single active substance was present, and in decaying it gave rise to an inactive substance, the phenomenon would be very simple. The radio-activity would diminish according to a simple exponential law ; *i.e.*, the same proportion of activity would disappear in equal times ; for example, half of the activity would always take the same time to disappear.

This law is represented by the equation $I = I_0 e^{-\lambda t}$. If the times are taken for abscissæ and the logarithms of the activities for ordinates, a straight line is obtained.

If, on the other hand, the substance A gives rise to another active substance B, and if this produces another substance C, also active, &c., the phenomena become much more complicated. Let us suppose that at first only the substance A exists ; it decays according to the above law, and the activity due to its presence will decrease according to a simple exponential. The quantity of the substance B is at first nil ; it increases as it is produced by A, and the production is proportional to the destruction of A. But B also disappears, and this disappearance is proportional to the quantity of B ; thus the quantity of B, and hence the activity due to its presence, will first increase, then reach a maximum, and finally decrease progressively. It may be shown that the law of the variation of the concentration of the substance B, and hence of its activity, can be represented by the difference of two exponentials, one characteristic of the destruction of A and the other characteristic of the destruction of B. For the variation of C we should get three exponentials, &c.

The total activity at each instant is equal to the sum of the activities, due respectively to the substances A, B, C, &c. ; *i.e.*, to the sum of exponentials with coefficients, the value of which depend on the activity of each substance.

* *Revue Générale des Sciences*, 1908, xix., 691.

TABLE I.—*Relations between Radio-active Substances.*

Substances.	Properties.	θ.	T.	Radiation.
Uranium	Atomic weight = 240. Iron group: soluble in ammonium carbonate; nitrate soluble in organic solvents.			$\alpha = 3{\cdot}3$ cm.
Uranium X	Iron group: carried down by $BaSO_4$; nitrate slightly soluble in organic solvents, acetone, ether, &c.	31·6 days	22 days	β
?				
Thorium	Atomic weight = 232. Precipitated by ammonia and oxalic acid.			α?
Mesothorium			5·5 years	β
Radio-thorium	Iron group.	1060 days	740 days	$\alpha = 3{\cdot}9$ cm.
Thorium X	Not precipitated by ammonia.	5·2 days	3·6 days	$\alpha = 5{\cdot}7$ cm.
Thorium emanation	Inert gas, condensible.	78 secs.	54 secs.	$\alpha = 5{\cdot}5$ cm.
Thorium A	Induced active deposit.	15·8 hours	11 hours	β, slow
Thorium B	Induced active deposit.	1·44 hours	1 hour	$\alpha = 5{\cdot}0$ cm.
Thorium C	Induced active deposit.	1·44 hours	Very short	$\alpha = 8{\cdot}6$ cm. β, γ
?				
Radium	Atomic weight = 226·5. Spectrum; group of alkaline earths. Continuously produces helium			$\alpha = 3{\cdot}5$ cm.
Radium emanation	Atomic weight by diffusion = about 100? Spectrum? Inert gas, condensible.	5·8 days	3·9 days	$\alpha = 4{\cdot}23$ cm.
Radium A	Induced active deposit.	4·3 mins.	3 mins.	$\alpha = 4{\cdot}83$ cm.
Radium B	Induced active deposit.	37·4 mins.	26 mins.	Slow β-rays
Radium C	Induced active deposit separated by electrolysis.	27·4 mins.	19 mins.	$\alpha = 7{\cdot}06$ cm. β, γ
Radium D	One of the constituents of radio-lead; properties very much like those of lead.	57·5 years	40 years?	No rays
Radium E	Separated from D by electrolysis.	8·6 days	6 days	β
Radium F or polonium	Sulphide insoluble in acids; precipitated with basic salts of bismuth; precipitated by stannous chloride.	201 days	140 days	α 3·86 cm.
?				
Actinium	Group of rare earths? Precipitated by oxalic acid and by hydrofluoric acid. Goes with neodymium and samarium in the fractionation of the ceric earths. Continuously produces helium.			No rays
Radio actinium	Separated by electrolysis and by fractionation with ammonia.	28 days	19·5 days	$\alpha = 4{\cdot}8$ cm.
Actinium X	Soluble in ammonia.	14·7 days	10·2 days	$\alpha = 6{\cdot}55$ cm.
Actinium emanation	Inert gas, condensible. Atomic weight = 70?	5·6 secs.	3·9 secs.	$\alpha = 5{\cdot}8$ cm.
Actinium A	Induced active deposit.	50 mins.	36 mins.	No rays
Actinium B	Induced active deposit. Separated by electrolysis.	2·9 mins.	2 mins.	$\alpha = 5{\cdot}5$ cm. β, γ
?				

The law of the variation of activity may thus be very complicated. However, the experimental decay curves have been analysed, and thus the number of active substances derived from one another has been deduced with certainty, and also the exponential constants characteristic of their decay. These decay curves are sometimes simplified; if, for example, the curve is represented by the difference between two exponentials of the form $Ke^{-\lambda t} - K'e^{-\lambda' t}$, where the coefficient λ is decidedly greater than λ', when t is increased the term containing $e^{-\lambda t}$ becomes, finally, very small, and thus the curve is reduced to a simpler exponential characteristic of one of the substances. Deducting the experimental curve of this exponential it is easy to obtain the second exponential. By this method Pierre Curie showed the differences of the exponentials in the case of the induced activity of radium, and thus deduced the elementary law of the phenomenon. Very valuable information can also be obtained by altering the initial conditions.

All these temporarily active substances can be distinguished from one another by means of other properties. In the first place the nature of the radiation; certain substances emit only α-rays, others β-rays, and others a mixture of α-, β-, and γ-rays; finally, certain substances do not emit rays or at most only a very feeble radiation.

Moreover, the researches of Bragg and Kleemann have shown that when a substance emits α-rays these rays are all of one kind; they all have the same range, which implies the same initial velocity of projection. The measurement of this range is comparatively easy, and by it certain active substances can be identified.

Finally, true separations can be effected either by physical or chemical processes. We have already seen that some substances are gaseous and that others are deposited on solid bodies. The gaseous emanations can generally be easily separated, either from solid salts or from solutions. They may even be condensed on solid walls by lowering the temperature sufficiently. Rutherford, who discovered this phenomenon, has shown that in the case of radium the condensation takes place within a small temperature interval; the condensation can be effected at the ordinary temperature on wood charcoal.

The different products which are included in induced radio-activity can also be separated by fractional distillation at a high temperature. Radium B and radium C can thus be nearly completely separated.

We have seen that chemical methods can be used to separate thorium X and actinium X; similar methods can be used to separate the constituents of induced radio-activity. Thus the active deposit of radium can be dissolved in an acid and then electrolysed. Radium C can thus be completely separated from radium B.

Do the chemical separations thus effected correspond exactly to the properties the substances would have if they could be obtained in ponderable quantities? This question is difficult to answer, but it must be admitted that the existence of these processes is in favour of Rutherford and Soddy's hypothesis that the phenomena of temporary activity are due to chemical substances; their existence is admittedly ephemeral, but during their short life they appear to possess well-defined chemical and physical properties.

Each active substance which disappears more or less rapidly may also be characterised by different properties, but it may be identified with certainty by the law of its spontaneous decay, which is determined exactly by the exponent λ; this exponent is the coefficient of velocity of the transformation. We know that in chemical reactions these coefficients of velocity are much influenced by external agents, temperature and pressure, and even by the presence of certain foreign bodies, catalysers. In radio-active transformations the coefficients of velocity seem to be absolutely independent of external conditions. For instance, Pierre Curie has shown that the velocity of the destruction of radium emanation does not vary from the temperature of liquid air to high temperatures.

This is a special characteristic of these phenomena, which is connected with the atomic nature of the property of radio-activity. Just as the nature of the atom and its mass are unaffected by the agents we are dealing with, the radio-active properties are not modified by external actions.

Instead of defining the law of the destruction of an active substance by the coefficient of velocity, it may be defined by a coefficient which has an interesting theoretical signification. If we consider the different atoms of an active substance in course of destruction, certain atoms will undergo the transformation at the end of a very short time; others, on the other hand, will have a much longer life; a mean duration of life of the different atoms can be deduced by employing the law of destruction. The quantity $\theta = 1/\lambda$ has been found for this mean duration of life, and θ is the coefficient generally used.

The law of transformation is very often defined by the interval of time, at the end of which half the substance is transformed; *i.e.*, at the end of which the activity due to the substance has diminished to one-half. These two constants are connected by the equation $T = \theta \log 2$.

For instance, for radium emanation $\theta = 136$ hours, $T = 92$ hours.

Many experiments were necessary to determine the succession of the different active substances derived from the principal substances known.

One of the most interesting results, chiefly due to Rutherford, is the proof that polonium, the activity of which as we have seen decreases slowly with time, may be connected with the radium series, and also that radio-lead is a mixture the different members of which are also derived from radium.

I append a table of different active substances the succession of which has been proved. The table includes four series, derived from uranium, thorium, radium, and actinium. For each substance I have given the interval of time corresponding to the half decay, the mean duration of life, the nature of the rays emitted with their range when it is known, and finally some information as to the physical and chemical properties which may be employed to separate them.

In a second article I shall continue the account of our present knowledge of radio-activity.

PRELIMINARY NOTE ON A NEW ELEMENT ALLIED TO MOLYBDENUM.

By MASATAKA OGAWA, Rigakushi.

Introduction.

IN the course of an examination of molybdenite in connection with my work on Nipponium, a substance, which was supposed to be ammonium vanadate, was obtained and set aside as such (*Journ. Coll. Sci., Imp. Univ.*, xxv., Art. 15, p. 7; CHEMICAL NEWS, xcviii., 249). A further examination of this substance has shown, however, that it is not ammonium vanadate, but that it is a compound of a new element, closely allied to molybdenum, and, indeed, associated with it in this compound; and although the results so far obtained are still very incomplete, they are now published in the hope that they may prove of sufficient interest.

It is possible and even likely that the "new tin-group element in thorianite," an account of which has been recently given by Miss Evans (*Journ. Chem. Soc.*, 1908, xciii., 666), is identical with this element, inasmuch as the latter has been found not only in molybdenite but also in thorianite, and two at least of the very few characteristic reactions ascribed to her element by Miss Evans, namely, the formation of a brown sulphide, insoluble in hydrochloric acid but soluble in hot nitric acid, and its solubility

* *Journal of the College of Science, Imperial University, Tokyo, Japan*, vol. xxv., Article 16.

in ammonium carbonate to form a deep brown solution, are likewise produced by the element now to be described. The formation of a golden-brown syrup on evaporation of a nitric acid solution of the sulphide, which she appears to regard as another characteristic of her element, could, however, in the case of the element forming the subject of this paper, be observed only with the impure sulphide, which, in some form or other, was found to contain a small quantity of iron, besides, perhaps, some other elements. Again, on reducing with hydrogen, the oxide prepared from such sulphide produced a metal, which, in agreement with Miss Evans' observation, was fusible at a bright red heat, but the metal obtained from the purified oxide was found to be non-fusible. It appears, therefore, that, if Miss Evans' element is really identical with mine, I have got it in a much purer state. In any case it is unfortunate that in consequence of her account being much too short no exact comparison can be instituted between the two. It is also unfortunate that, in spite of her positive statement as to the existence of molybdenum in thorianite, she does not tell us how this element has been completely removed, the sulphide of molybdenum also dissolving in ammonium carbonate to form a deep brown solution.

There is one other point which should be noted before going further. Miss Evans says that the sulphide of her element is soluble in water. The solubility of the sulphide upon which I worked may be inferred from the fact that one of its sources was the sulphide residue from thorianite, which had escaped precipitation by hydrogen sulphide (see *prox.*), and also from the fact that a solution of the purified oxide in ammonia was almost completely precipitated by hydrogen sulphide, *only* after acidification and *on boiling*. The presence of the element in the filtrate from the hydrogen sulphide group may therefore be most probably ascribed to the incomplete heating during precipitation by hydrogen sulphide.

Preparation from Molybdenite of a Compound containing the New Element and its Examination.

As the condition under which the supposed ammonium vanadate was previously obtained was such that it did not ensure its separation quantitatively and in the pure state, supposing it to be really ammonium vanadate, the following procedure has been adopted. After igniting in oxygen the powdered mineral was extracted with ammonia. The residue, still containing some unaltered mineral, was repeatedly boiled with concentrated nitric acid, and the whole evaporated to dryness and again extracted with ammonia. The final residue, on digestion with ammonium sulphide, gave a deep reddish brown solution, which was filtered from the insoluble portion containing the sulphides of lead, bismuth (?), iron, nipponium, and zinc, and the hydroxide of aluminium. The dark brown precipitate, obtained on acidifying the solution with hydrochloric acid and heating, was decomposed with nitric acid, and the yellowish brown syrupy residue, left on evaporation of the nitric acid solution, ignited in the air. The dark brown residue thus obtained was fused with potassium nitrate, and the fused mass extracted with water, when a small quantity of a reddish brown substance, consisting chiefly of ferric oxide, was left undissolved. The aqueous alkaline extract was neutralised with nitric acid and, after concentration, mixed with an equal volume of a saturated solution of ammonium chloride, followed by the addition of one-third of the total volume of 90 per cent alcohol. A crystalline precipitate, apparently the same as that which had been previously obtained and set aside as ammonium vanadate, was produced on standing for some time, and this was washed, first with a saturated solution of ammonium chloride and then with dilute alcohol.

Judging from the mode of procedure no other known substance but ammonium vanadate could have come down as a crystalline precipitate under the conditions above detailed, but the reactions described below clearly show that it is not ammonium vanadate. Neither can it be ammonium molybdate, for this salt is not known to be precipitated by ammonium chloride. It is true that the compound gives some of the reactions of molybdenum, which it undoubtedly contains in one form or another, but the fact above alluded to, that it has been obtained under conditions which exclude the possibility of ammonium molybdate being precipitated pure and simple, makes it exceedingly probable either that the compound above obtained is a complex salt containing molybdenum and the new element or that it belongs to the class of mixed crystals.

The yield of the compound was about 7 grms. from 400 grms. of molybdenite. It is remarkable that the existence, in this mineral, of such a comparatively large amount of a new element should have hitherto escaped observation, but this may be explained by the fact that the element is very closely allied to molybdenum and that its equivalent weight does not differ much from that of the latter.

Properties of the Compound.—The compound above obtained, which is evidently an ammonium salt, crystallises in minute prisms, easily soluble in water, and its aqueous solution gave the following reactions :—

(1) Hydrogen sulphide, in presence of hydrochloric acid, only gave a brown coloration without producing any precipitate, but on heating the solution to boiling a dark brown precipitate was formed (difference from a vanadate, which is not precipitated by hydrogen sulphide either in the cold or when heated), the filtrate from it being quite colourless (difference from a molybdate, which gives a blue coloured filtrate).

(2) On reducing the solution with zinc and hydrochloric acid no colour appeared for some time, but on standing a blue colour changing to brown was produced ; at the same time a substance having a metallic lustre adhered to the zinc. A solution of pure ammonium molybdate of the same concentration similarly treated at once turned blue, ultimately changing to brown, and the brown solution on long standing deposited a dirty brown amorphous substance.

(3) Barium chloride, lead acetate, silver nitrate, and mercurous nitrate all gave precipitates, soluble in nitric acid and similar in appearance to the respective salts of molybdic acid, except the mercurous salt. The barium salt forms a white crystalline powder, slightly soluble in water ; the lead salt is a white amorphous powder, insoluble in water ; the silver salt forms a pale yellow precipitate, slightly soluble in water ; and the mercurous salt consists of golden yellow crystals, insoluble in water. Mercurous molybdate is obtained, under like conditions, as a white or pale yellow amorphous substance. (Struve has observed that the milky precipitate of mercurous molybdate changes into golden yellow needles through prolonged washing or on standing.—*Journ. Prakt. Chem.*, lxi., 467, quoted in Dammer's "Handbook der Anorg. Chem., III., 628).

(4) After strongly acidifying the solution with nitric acid sodium phosphate gave a compound apparently similar to ammonium phosphomolybdate.

(5) In presence of potassium thiocyanate, zinc and hydrochloric acid gave a blood-red coloration.

Besides the above described reactions, which were observed with an aqueous solution of the salt, the following must also be mentioned.

(6) The residue obtained on heating the ammonium salt and consisting of the oxide, either alone or mixed with molybdenum trioxide, did not possess the characteristic yellowish red colour of vanadium pentoxide, but was similar in appearance to molybdenum trioxide and slowly volatilised at a red heat, becoming crystalline at the same time. It produced a deep blue coloration on heating with concentrated sulphuric acid.

(7) The oxide, when heated in a current of hydrogen gas, was reduced into the metal, which was non-fusible at a bright-red heat, and the metal could be easily brought back into the oxide by heating it in the air. The equivalent weight of the metal was determined both by reducing the oxide into the metal and by converting the metal back

into the oxide; the values obtained were 16·4 and 16·6, not very far from the equivalent weight of molybdenum.

Thinking that the ammonium salt above obtained might be a mixture of two salts, one containing molybdenum and the other the unknown element, an attempt was made to separate them, if possible, by fractional crystallisation. For this purpose the salt was again prepared according to the method already described, collecting, however, one crop of crystals shortly after the addition of ammonium chloride and without using alcohol, and another crop after adding alcohol to the mother-liquor and allowing it to stand for two days. From these two fractions, which looked exactly alike, water of crystallisation, ammonium oxide, and the residual oxide or oxides were determined with practically the same results.

The attempt which was next made to prepare the sodium salt resulted in showing the compound nature of the ammonium salt. The oxide obtained from the ammonium salt was fused with an equivalent quantity of sodium carbonate, calculated from the equivalent weight already determined on the supposition that the sodium salt would have the composition Na_2XO_4; the fused mass was dissolved in water and the solution evaporated, when hygroscopic crystals were obtained. Under a microscope these were found to consist partly of thin plates and partly of small needles, but, owing to their hygroscopic nature, their mechanical separation was found to be impossible.

Isolation of the element was at last effected through the electrolysis of the ammonium salt. On electrolysing an aqueous solution of the ammonium salt at a temperature of 60° to 70°, using a current density of 1 ampere per 100 sq. cm. and a potential difference of 4 volts, a black substance deposited on the cathode. It was found to contain molybdenum, doubtless as a hydrated sesquioxide, and on heating it with 2N-hydrochloric acid the molybdenum compound gradually dissolved away to form a dark brown solution. Treatment with hydrochloric acid was repeated until the fresh acid was no longer coloured brown. A portion of the residue (hydrated lower oxide of the new element ?), which was graphitic in appearance was boiled with nitric acid, the whole evaporated to dryness and extracted with ammonia. The ammoniacal solution was also evaporated to dryness and the residue dissolved in water. This aqueous solution gave all the reactions previously described, with the exception of the colour reactions mentioned in (2), (5), and (6), but these reactions are exactly those which are characteristic of molybdenum. It is true that a faint coloration was produced with zinc and hydrochloric acid in presence of potassium thiocyanate, but so faint that, considering the delicacy of this colour reaction, we may reasonably believe that almost every trace of molybdenum has been removed, and that the new element, or rather its oxide or the hydrated oxide, has been obtained in an almost pure state.

Properties of the Element.—The supposed new element, obtained by heating the above described graphitic substance in a current of hydrogen gas, has a metallic lustre and looks somewhat like magnesium powder. It burns brilliantly when heated in the air, producing the oxide, a part of which volatilises at the same time. The oxide, when heated in hydrogen gas, reproduces the metal in the form, however, of a grey powder resembling molybdenum, produced under like conditions. It is non-fusible at a red heat. On prolonged boiling it dissolves in concentrated hydrochloric acid, producing a faint greenish yellow solution. In this latter respect it is distinguished from molybdenum, which is insoluble in the acid. The hydrochloric acid solution on evaporation to dryness at 100° gives a white residue of the chloride, soluble in water. This residue, on ignition, becomes difficultly soluble, doubtless due to its conversion into the oxide or the oxychloride.

The equivalent weight was again determined, using the purified metal. (1) 0·1464 grm. of the metal gave 0·2149 grm. of the oxide, from which the number 17·1 was calculated. (2) 0·2149 grm. of the oxide gave 0·1451 grm. of the metal, which led to the value 16·7. Of these two results, the lower value, 16·7, which was obtained from the reduction of the oxide, must be regarded as more exact, there being an unavoidable slight loss by volatilisation of the oxide produced, when the metal is heated in the air, however carefully the heating be conducted. The reduction of the oxide can, on the contrary, be carried on with perfect safety, a lower oxide which is non-volatile at full red heat being, apparently, formed during the first stage of the reduction, so that if the heating is regulated at the beginning there is no danger of any loss being incurred.

The atomic weight of the element becomes 100, if calculated from the equivalent weight on the supposition that it is hexavalent like molybdenum. But the number 100 is that already given to nipponium as its atomic weight (*loc. cit.*), and nipponium differs from the element now under consideration in its oxide not being reducible by hydrogen and in other respects. It is possible that nipponium, instead of being divalent, as was supposed, may prove to be a trivalent element, with an atomic weight of 150, but discussion on this point, as well as on the atomic weight of the new element, will be reserved until the specific heat determinations of the two elements now being undertaken by Prof. Ikeda, of the Science College, and my analyses of their different compounds, shall have been completed.

It may be here stated, by way of parenthesis, that a new rich source of nipponium has been discovered. On carefully examining samples of thorianite there have been found here and there small, translucent, prismatic crystals, varying in colour from yellow to red. They are very hard and can scratch glass quite easily. The specific gravity of the mineral is 4·5, being about one-half of that of thorianite. This mineral was once thought to be zircon, but on further examination it has been found that it is a double silicate of zirconium and nipponium, and about 50 grms. of it have been picked out from 5 kilogrms. of thorianite. It is hoped that several grms. of nipponium may now be obtained from this source, about a grm. of the metal having been already prepared by the electrolysis of the double fluoride of nipponium and potassium.

Examination of the Sulphide Residue from Thorianite.

While in University College, London, Sir William Ramsay gave me for investigation 1½ kilogrms. of crude hydrogen sulphide precipitate obtained from 5 cwt. of thorianite. This was ignited in the air, fused with hydrogen potassium sulphate, extracted with water, and re-precipitated by hydrogen sulphide. The filtrate from the precipitated sulphides was treated as in the ordinary course of analysis, and the solution, after the iron-group precipitate had been removed, had a deep reddish brown colour. It did not, however, produce any precipitate with ammonium sulphide, but the colour was suspected to be due to the presence of an unknown element. The sulphur, separated out from the solution on the addition of hydrochloric acid after ammonium sulphide had been added, was found to possess a deep brown colour and to leave a brown residue on ignition. About 100 grms. of this sulphur have been brought with me to Japan, and recently examined with the following results.

On ignition the sulphur gave about 8 per cent of the residue. This was repeatedly extracted with hot concentrated nitric acid, and it was found that the first portions of the extract had a bluish green and the later portions a reddish brown colour. Treatment with nitric acid was continued until no more colour was imparted to it, but a considerable fraction of the brown residue was still left undissolved.

The colour of the first portions of the extract was somewhat like that of a cupric salt, but that it was not due to the presence of this element was shown by the fact that the dark brown—almost black—precipitate produced by sodium sulphide, after nitric acid had been evaporated off, was completely dissolved by an excess of the reagent.

The sulphide, re-precipitated from the solution on the addition of hydrochloric acid, was moistened with concentrated nitric acid and ignited, and then fused with potassium nitrate. The brown residue left on extracting the fused mass with water was found to consist of an unknown oxide mixed with ferric oxide, it being this unknown oxide which dissolves in nitric acid with a bluish green colour. The aqueous extract did not contain any molybdenum, but it did contain the same new element as occurs in molybdenite, forming the subject of the present paper, as was shown by the formation of a brown sulphide, soluble in ammonium carbonate to form a deep brown solution, the precipitation of the salts of barium, lead, and silver, and more especially of the characteristic mercurous salt, as well as by the volatility and the crystalline nature of the oxide obtained from it.

The later portions of the nitric acid extract, which had a reddish brown colour, were evaporated to dryness, when a deliquescent, gummy mass of a brown colour was left behind. On ignition and subsequent fusion with potassium nitrate it was found to be resolved into the same three constituents as were obtained from the first portions of the nitric acid extract, namely, ferric oxide and the unknown oxide in the residue, after extracting the fused mass with water, this unknown oxide dissolving in nitric acid to form a bluish green solution, and the oxide of the new element in the aqueous extract. It must be here remarked that, although the nitric acid extracts, both green and brown, undeniably contain iron, as is shown by their subsequent treatment, they give no reactions with potassium ferrocyanide.

With regard to the unknown oxide, which dissolves in nitric acid with a bluish green colour, above referred to, no further observation has been made than that it is radio-active, and it is likely that the radio-activity of the sulphide residue from thorianite is due to the presence of this substance. It can be definitely stated that it does not contain any uranium. Since the brown coloured nitric acid extracts also give the same unknown oxide, dissolving in nitric acid with a bluish green colour after fusion with potassium nitrate, it is possible that the difference in colour may be due to the existence of two different oxides of one and the same unknown element.

Conclusions.

1. Both molybdenite and thorianite contain a new element, which is closely allied to molybdenum.

2. It forms a complex salt (?) with ammonium molybdate, precipitable, from its aqueous solution, in a crystalline form on saturation with ammonium chloride.

3. It appears to form two different oxides, the higher oxide being similar in its properties to molybdenum trioxide and acting as an acidic oxide. The salts of barium, lead, and silver formed from the higher oxide resemble the corresponding molybdates, but the mercurous salt consists of golden-yellow crystals.

4. The hydrated lower oxide (?) has a graphitic appearance, and is insoluble in hot dilute hydrochloric acid.

5. On heating in a current of hydrogen gas, either of the oxides produces the metal, which is non-fusible at a red heat. It burns brilliantly in the air, producing the higher oxide.

6. The equivalent weight of the metal is somewhat above that of molybdenum, being about 16·7.

7. In producing a brown sulphide and in other respects, above referred to, the new element resembles molybdenum, but is distinguished from the latter in producing no colour reactions, when a soluble salt of its higher oxide is reduced with zinc and hydrochloric acid, either in the presence or absence of potassium thiocyanate, and also by the fact that the metal dissolves in hot concentrated hydrochloric acid.

8. The "new tin-group element," recently described by Miss Evans, is probably identical with the element forming the subject of this paper.

9. A new rich source of nipponium has been discovered and, incidentally, described.

10. Besides nipponium and the new element now under consideration, thorianite appears to contain still another new element, the oxide of which is radio-active and dissolves in nitric acid to form a bluish green solution.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

PART III.—ANALYSIS OF THE ALUMINIUM AND IRON GROUPS, INCLUDING BERYLLIUM, URANIUM, VANADIUM, TITANIUM, ZIRCONIUM, AND THALLIUM.

By ARTHUR A. NOYES, WILLIAM C. BRAY, and ELLWOOD B. SPEAR.

(Continued from p. 252).

Confirmatory Experiments and References (continued).

Delicacy of the Confirmatory Test for Chromate.—To a solution containing 0·5 cc. Cr as K_2CrO_4 in 100 cc. was added a little ammonium acetate solution, 2 cc. acetic acid, and 1 grm. $BaCl_2$: a yellow precipitate separated at once. This was collected on a filter, and treated by P. 56: upon the addition of H_2O_2 and ether, a distinct blue colour resulted. The experiment was repeated with 0·2 mgrm. Cr: a slight but distinct precipitate and colour were obtained.

Reduction of Chromic Acid by Filter-paper.—10 mgrms. Cr as K_2CrO_4 were precipitated as lead chromate, and the mixture filtered. The precipitate, with the filter, was placed in a casserole; 10 cc. water and 5 cc. HNO_3 (1·20) were added, and the mixture was boiled. The solution turned green in about one minute, thus showing that reduction takes place readily.

P. 57, N. 3: *Ignition Test for Zinc with Cobalt Nitrate.*—0·1, 0·2, and 10 mgrms. Zn as $Zn(NO_3)_2$ were treated as described in the second paragraph of P. 57, 0·2 mgrm. Co as nitrate being used in each experiment: a distinct green colour resulted in the experiment with 0·1 mgrm. Zn, a deeper colour with 0·2 mgrm. and an intense colour with 10 mgrms. 1 mgrm. Zn and 2 mgrms. Co as nitrates were treated as described in the last paragraph of P. 57: the residue was green. The residue was then heated strongly: it turned black, showing that when an excess of cobalt is present the test is more delicate if the mixture is not heated strongly. The experiment was repeated with 2 mgrms. Cr and 1 mgrm. Zn: a green colour resulted which remained after the residue had been heated strongly.

A solution containing 5 mgrms. Zn and 0·5 mgrm. Co as nitrates was evaporated to dryness in a casserole and the mixture was ignited, first gently and then strongly: the residue was black owing to the presence of cobalt oxide. 0·3 mgrm. Zn and 0·2 mgrm. Co as nitrates were treated by the last paragraph of P. 57, except that 5 cc. of 10 per cent Na_2CO_3 solution were added in excess: only a very faint green colour resulted. The experiment was repeated except that only 3 drops Na_2CO_3 solution were added in excess; the green colour was mixed with black. The experiment was repeated, with an excess of 1 cc. and also with an excess of 0·5 cc. Na_2CO_3 solution: a good green colour was obtained. These experiments show that some Na_2CO_3 must be added, but only a moderate quantity.

A solution containing 0·3 mgrm. Zn and 0·2 mgrm. Co as chlorides and an excess HCl was treated by P. 57 (last par.), no HNO_3 being added: the residue had no distinct colour, showing that HCl cannot be substituted for HNO_3.

*P. 58*a*, N. 3: *Composition of the Zinc and Beryllium Precipitates produced by Sodium Hydrogen Carbonate.*—500 mgrms. Zn as nitrate were treated by *P. 58*a*, using a total volume of 100 cc. The precipitate was carefully washed with water, and tested for carbonate in the usual way by treating with acid in a flask and passing the gas

* From the *Journal of the American Chemical Society*, XXX., No. 4.

evolved through $Ba(OH)_2$ solution. A large precipitate of $BaCO_3$ was obtained which corresponded to at least 200 to 300 mgrms. Zn. The experiment was repeated with 200 mgrms. Be: a large amount of carbonate was also found in the beryllium precipitate, the precipitate of $BaCO_3$ being about twice as large as in the experiment with zinc. Parsons states (*Journ. Am. Chem. Soc.*, 1906, xxviii., 557) that the precipitate obtained in a dilute ammonium carbonate solution is a basic carbonate of beryllium.

Precipitation of Aluminium in Hot Sodium Hydrogen Carbonate Solutions in a Closed Bottle.—Solutions containing 2 mgrms. Al as nitrate in 100 cc. were placed in pressure bottles, and 2, 5, and 10 mgrms. $NaHCO_3$ added: each of the three solutions quickly became turbid in the cold. The bottles were heated at about 95° in a water-bath for half an hour: a flocculent precipitate formed in each case in less than five minutes, and settled in less than twenty minutes. The bottles were cooled and the precipitates filtered off; the filtrates were evaporated with excess of HNO_3 and tested for aluminium with NH_4OH: little or no precipitate separated, showing that the precipitation of the aluminium had been practically complete in each case. The experiments were repeated with 1, $\frac{1}{4}$, $\frac{1}{16}$, and $\frac{1}{32}$ grms. $NaHCO_3$; the results were the same except that the precipitation was not complete with $\frac{1}{32}$ grm. $NaHCO_3$. The experiment was repeated with $\frac{1}{64}$ grm. $NaHCO_3$; no precipitate was obtained. These experiments were repeated, except that the solution was thoroughly saturated with CO_2 gas before adding the $NaHCO_3$; the results were nearly the same.

A solution containing 500 mgrms. Al as nitrate in 100 cc. was placed in a bottle and 4 grms. $NaHCO_3$ added; there was a violent evolution of CO_3 gas, a small precipitate formed, and the solution still reacted acid to litmus. One grm. more $NaHCO_3$ was added; a very large precipitate separated, very little gas came off, and the solution after shaking did not turn blue litmus red. The mixture was heated in the closed bottle at 95° in a water-bath for half an hour, cooled, and filtered; the filtrate was found to contain no aluminium. Therefore 500 mgrms. Al are completely precipitated when about 5 grms. $NaHCO_3$ are added in 100 cc. of solution.

Precipitation of Zinc Carbonate in Hot Sodium Hydrogen Carbonate Solutions.—Four solutions, each containing 2 mgrms. Zn as nitrate dissolved in 100 cc., were poured into strong 200 cc. bottles; to these were added 1, 2, 3, and 5 grms. respectively of solid $NaHCO_3$: the bottles were corked and shaken until the $NaHCO_3$ dissolved; they were then heated in a water-bath at 90° to 95° for half an hour; all the solutions became slightly turbid in the cold and after heating for five minutes precipitates could be seen in suspension. After the half hour's heating the bottles were allowed to cool to about 40°, and the solutions containing 1 and 5 grms. $NaHCO_3$ were filtered and tested for zinc by evaporating with HNO_3, adding NH_4OH and acetic acid, and passing in H_2S; only a trace of zinc was found in each filtrate, thus showing that the precipitation was practically complete in both 1 per cent and 5 per cent $NaHCO_3$ solutions. The experiments with 1 and 2 grms. $NaHCO_3$ were repeated except that the solutions were thoroughly saturated with CO_2 gas at room temperature before the $NaHCO_3$ portions were added: the results were the same.

The experiment was repeated with a solution containing 500 mgrms. Zn as nitrate in 100 cc., 2 grms. $NaHCO_3$ being added; no precipitate of ZnS separated. The experiment was repeated with 500 mgrms. Zn and 1·5 grms. $NaHCO_3$; about 5 mgrms. Zn were found in the filtrate, showing that 1·5 grms. $NaHCO_3$ is not quite sufficient to precipitate 500 mgrms. Zn completely.

Precipitation of Beryllium in Hot Sodium Hydrogen Carbonate Solutions in a Closed Bottle.—A solution containing 1 mgrm. Be as nitrate in 100 cc. was placed in a 200 cc. bottle, 1 grm. $NaHCO_3$ was added, and the mixture was digested in the tightly stoppered bottle at about 95° in a water-bath for half an hour; the solution became turbid in less than five minutes and a precipitate separated in ten minutes; on standing in the cold for an hour the precipitate seemed to re-dissolve to a small extent. The experiment was repeated with a solution that was saturated with CO_2 gas before the $NaHCO_3$ was added; the result was the same. These experiments were repeated with 1 mgrm. Be and 2 grms. $NaHCO_3$; the mixture that had been saturated with CO_2 was distinctly turbid in fifteen minutes, while the other was only very slightly turbid after half an hour. The solutions cleared on standing for an hour in the cold. The last experiments were repeated with 2 mgrms. Be and 2 grms. $NaHCO_3$: distinct precipitates were obtained corresponding to about 1 mgrm. Be, but these re-dissolved to a considerable extent in the cold.

These experiments were repeated with solutions containing 3 to 10 grms. $NaHCO_3$ in 100 cc. of solution and varying quantities of beryllium; in the 3 per cent $NaHCO_3$ solution 3 mgrms. Be gave no precipitate, but a larger amount did so; in the 5 per cent solution, about 15 mgrms. Be just remained in solution in 100 cc.; and in the 10 per cent solution, about 75 mgrms. Be gave a small precipitate in 50 cc., while 50 mgrms. Be gave only a negligible precipitate.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 5th, 1908.

Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

Mr. G. J. Fowler was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Thomas James Baker, D.Sc., Trebarwith, Chester Road, Erdington, Birmingham; Charles Everitt, M.A., 67, Boston Avenue, Southend-on-Sea; Henry Hamilton Green, 36, Princes Square, Regent Park, Glasgow; Edward Hinks, B.Sc., 23, Tavistock Road, Croydon; Joseph Kenyon, B.Sc., 6, Cheltenham Street, Blackburn; Gregor MacGregor, M.A., B.Sc., Giffen Park, Dysart, Fife; William Herbert Miles, 3, Liversidge Road, Higher Tranmere, Birkenhead; Charles James Millar, care of Messrs. Turner, Morrison, and Co., Calcutta; George Edward Pearson, care of Messrs. Burroughs, Wellcome, and Co., Snow Hill Buildings, E.C.; Frank Moreton Thomas, 290, Rotton Park Road, Edgbaston Birmingham; Sidney Gilbert Walton, "Kensington," Northwood Road, Northwood, Lane Cove River, N.S.W.; William Crd Wootton, B.Sc., 159, Maidstone Road, Rochester; Frederick Palliser Worley, M.A., M.Sc., Mansfield House, Clifton Gardens, Maida Hill, W.

Of the following papers, those marked * were read:—

*221. "*The Direct Union of Carbon and Hydrogen. Synthesis of Methane*," By William Arthur Bone and Hubert Frank Coward.

The recent work of Berthelot, Pring and Hutton, and Mayer and Altmayer on this subject was critically reviewed. The results of new experiments were described which demonstrate the formation of large quantities of methane when less than 0·1 grm. of sugar-charcoal (highly purified by prolonged ignition in dry chlorine, first of all at 700° and then at 1100°) is heated in a stream of pure dry hydrogen to between 1100° and 1200° in an apparatus similar to that used by Bone and Jerdan in 1897.

In two separate experiments, the yields of methane (namely, 137·0 cc. and 125·5 cc. at 0° and 760 mm. from 0·0995 and 0·092 grm. of carbon respectively) were as much as 73 per cent of those theoretically obtainable, the

remainder of the methane being lost by unavoidable oxidation or decomposition in contact with the intensely hot walls of the porcelain tube in which the carbon was heated. In one group of four experiments, the formation of altogether 422 cc. of methane from 0·306 grm. of carbon was demonstrated. The authors therefore consider that the synthesis of methane from its elements, as originally carried out by Bone and Jerdan in 1897 and 1901, is fully confirmed.

Incidentally, the results of analyses of the sample of highly purified carbon originally used by Bone and Jerdan were given, showing that the hydrogen in it did not exceed 0·06 per cent, of which at least part would be occluded.

DISCUSSION.

Dr. LOWRY, as evidence of the unreliability of thermo dynamic calculations of high temperature equilibria, referred to the case of nickel oxide, where the pressure of oxygen at 1127° had been calculated by Stahl (*Metallurgie*, 1907, iv., 682) as 0·000000033 mm., the values actually observed (Foote and Smith, *Journ. Am. Chem. Soc.*, 1908, xxx., 1349) being 5·5 mm. at 1100° and 13·0 mm. at 1200°. The value calculated for 227° was $1·859 \times 10^{-45}$, or roughly $0·5 \times 10^{-21}$ molecule per 22·4 litres, and in the case of zinc oxide, $1·333 \times 10^{-67}$ or $0·3 \times 10^{-43}$ molecule, figures which, in spite of the formal exactness, were of such ultra-electronic minuteness as to have no significance whatever.

Dr. FEILMANN asked whether Prof. Bone could supply information as to the black substance formed by the methane on the walls of the porcelain tube in which the reaction took place, and suggested that it might contain carbon, due to decomposition of the methane formed; such decomposition might be promoted both by the walls of the tube being presumably rather hotter than the body of the gas, and also by the special action which was well known to be peculiar to solid surfaces in similar circumstances. It was difficult to believe that the coloration could be due to the formation of silicon in the porcelain, and it presumably contained no lead.

Prof. BONE, in reply, wished it to be understood that he did not attack Nernst's thermodynamical arguments as being, from the abstract point of view, unsound—this not being the point raised in the paper—but merely contended that for calculating high temperature equilibria they were at present useless, owing to defective knowledge of the measure of the thermal factors involved. There was nowadays a tendency, in certain quarters, to over-estimate the value of mathematical deductions in relation to chemical phenomena, and it was necessary to protest against the practice of setting aside the results of carefully conducted experiments on merely mathematical grounds.

In answer to Dr. FEILMANN, he was afraid he could give no definite information as to what particular constituent of the porcelain or the glaze of the inner tube had been reduced by the methane; presumably it might be the silica, and certainly the appearance of the tube suggested this. With regard to the mechanism of the process, it might be either a direct reduction by methane itself, or a secondary effect due to carbon liberated by a primary decomposition of methane in contact with the hot surface.

*222. "*The Relation between Absorption Spectra and Chemical Constitution.* Part XI. *Some Aromatic Hydrocarbons.*" By EDWARD CHARLES CYRIL BALY and WILLIAM BRADSHAW TUCK.

The authors have examined the absorption spectra of the following hydrocarbons:—Naphthalene, acenaphthene, acenaphthylene, fluorene, chrysene, anthracene, phenanthrene, diphenyl, and dibenzyl. Certain minor differences from Hartley's observations of naphthalene, anthracene, and phenanthrene (*Trans.*, 1881, xxxix., 153; 1885, xlvii., 685) have been noted. In some cases the absorption of the hydrocarbons shows considerable similarity among themselves, from which it has been found possible to gain some insight into the dynamic condition of these substances.

*223. "*Organic Derivatives of Silicon.* Part VII. *The Synthesis of* dl-*Sulphobenzylethyl*iso*butylsilicyl Oxide.*" By BERNARD DUNSTAN WILKINSON LUFF and FREDERIC STANLEY KIPPING.

The only optically active silicon compounds which have hitherto been described, namely, the *d*- and *l*- forms of sulphobenzylethylpropylsilicyl oxide, $SO_3H{\cdot}C_6H_4{\cdot}CH_2{\cdot}SiEtPr{\cdot}O{\cdot}SiEtPr{\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3H$, have very low specific rotations, and in many cases when they are combined with a given optically active base their enantiomorphous relationship is not very clearly indicated.

Although there can be no doubt that the molecules of these acids are asymmetric, it seemed desirable to prepare, if possible, some other compound of the same type. With this object, the authors have synthesised *benzylethyl*iso*butylsilicyl chloride*, $SiEt(C_7H_7)(C_4H_9)Cl$, b. p. 198 — 202° (100 mm.); *benzylethyl*iso*butylsilicol*, $SiEt(C_7H_7)(C_4H_9){\cdot}OH$, b. p. 162—164° (25 mm.), and *benzylethyl*iso*butylsilicyl oxide*, $[SiEt(C_7H_7)(C_4H_9)]_2O$, b. p. 250—252° (20 mm.). Each of these three substances was then sulphonated with the aid of chlorosulphonic acid, and also in the case of the silicol and the oxide with concentrated sulphuric acid. The product in all cases was a mixture from which the same *dl*-acid, namely, dl-*sulphobenzylethyl*iso*butylsilicyl oxide*, was isolated in the form of its *l*-*menthylamine* salt; this compound, $[SiEt(C_4H_9){\cdot}CH_2{\cdot}C_6H_4{\cdot}SO_3H]_2O,2C_{10}H_{21}N,4H_2O$, melts at 240—245°, and its specific rotation is $[\alpha]_D$ −14·7° in methyl-alcoholic solution; it is not resolved by fractional crystallisation.

From the *l* menthylamine derivative, the *sodium* salt of the pure *dl*-acid was obtained, and from the latter the d-*bornylamine*, *cinchonidine*, and *cinchonidine hydrogen* salts were prepared.

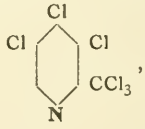
Experiments on the resolution of this *dl*-acid will be described at an early date.

*224. "*The Relation between Viscosity and Chemical Constitution.* Part III. *The Enol-ketonic Tautomerism.*" By ALBERT ERNEST DUNSTAN and JAMES ARTHUR STUBBS.

The authors have investigated the viscosity of ethyl acetoacetate, ethyl ethylacetoacetate, and ethyl diethylacetoacetate, alone and in various solvents. They have also studied the effects of piperidine and sodium ethoxide on ethyl acetoacetate. In confirmation of the work of Brühl, Perkin, Drude, Schaum, Knorr, and Lowry on these and similar compounds, they conclude that ethyl acetoacetate is mainly existent in the ketonic condition.

225. "*The Chlorination of Methyl Derivatives of Pyridine.* Part II. 2-*Methylpyridine.*" By WILLIAM JAMES SELL.

When α-picoline hydrochloride saturated with hydrogen chloride is chlorinated at 105—110° until no further action is apparent, an oily mixture of chlorinated derivatives is obtained, which, on the removal of the excess of chlorine and hydrogen chloride by a current of dry air, partly solidifies. The solid compound thus obtained was shown (Part I., *Trans.*, 1905, lxxxvii., 799) to have the constitutional formula:—



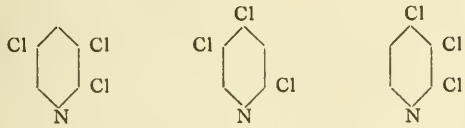
and the author has now examined the liquid part of the products. The chief constituent of this oily liquid is *pentachloropicoline*, $C_5H_2Cl_2N{\cdot}CCl_3$. This compound readily yields 3 : 5-*dichloropicolinic acid*, which crystallises from water in needles melting at 153—154°. The *methyl* ester and the *amide* have been prepared. On heating, the acid is converted into 3 : 5-*dichloropyridine*, m. p. 66—67°.

226. "*The Chlorine Derivatives of Pyridine.* Part IX. *Preparation and Orientation of* 3 : 5-*Dichloropyridine.*" By WILLIAM JAMES SELL.

The well-marked basic characters of this substance, together with its great stability, suggested that the chlorine atoms in this compound occupy the 3 : 5-position. This conclusion is strengthened by the analogy in general properties and stability under similar conditions to the dibromopyridine, m. p. 110—111°, in which the bromine atoms are known to occupy the positions 3 : 5. The orientation was carried out by converting specimens of the 3 : 5-dibromopyridine and the dichloropyridine in question into diethoxypyridine, and showing that the diethoxypyridines from the two sources yield identical compounds with bromine and with chlorine.

227. "*The Chlorine Derivatives of Pyridine.* Part X. *Orientation of* 2 : 3 : 5-*Trichloropyridine.*" By William James Sell.

Excluding the trichloropyridines of known constitution, and having regard to the feeble, but distinct, basic properties of the compound in question, there seemed every probability that its constitution should be represented by one of the following formulæ :—



I. II. III.

of which I. was regarded as sufficiently probable to warrant the attempt to determine its constitution on the following lines :—

Such a compound ought to be attacked by ammonia, giving 3 : 5-dichloro-2-aminopyridine. This was carried out, and a substance melting at 84—85° was isolated. Further, 3 : 5-dichloropicolinamide (*Proc. Chem. Soc.*, xxiv., 225) was converted by the Hofmann reaction into 3 : 5-dichloro-2-aminopyridine.

The compound thus prepared melted at 84—85°, and the melting-point was unaffected by admixture with the specimen obtained by the action of ammonia on the trichloropyridine in question. Moreover, Königs and Geigy have described (*Ber.*, 1884, xvii., 589, 1833) a dichloroethoxypyridine obtained from this trichloropyridine by the action of sodium ethoxide. This substance was converted into the dichlorohydroxypyridine, m. p. 178°, by heating with hydrochloric acid.

Finally, 3 : 5-dichloro-2-aminopyridine was converted by a modification of the Bouveault reaction into the same dichlorohydroxypyridine, m. p. 178—179°, as was obtained from the trichloropyridine in question.

228. "*The Triazo-group.* Part V. *Resolution of* α-*Triazopropionic Acid.*" By Martin Onslow Forster and Hans Eduard Fierz.

l-α-*Triazopropionic acid*, $CH_3 \cdot CHN_3 \cdot CO_2H$, has the specific gravity 1·2293 compared with water at 21°, and $[\alpha]_D$ −2·27°; a 16 per cent solution in ether has $[\alpha]_D$ −28·9°, and a 21 per cent solution in water, $[\alpha]_D$ +4·8°. The *brucine* salt, $C_{26}H_{31}O_6N_5$, has not a definite melting-point, but evolves gas at about 150°; the aqueous solution displays mutarotation, the permanent value being $[\alpha]_D$ −26·4° in a concentration of 4 per cent. The *ethyl* ester, $C_5H_9O_2N_3$, boils at 49° under 5 mm. pressure, has specific gravity 1·063 compared with water at 22°, and $[\alpha]_D$ −18·2°; the *amide*, $C_3H_6ON_4$, melts at 85°, and is dextrorotatory, having $[\alpha]_D$ 49·1° in water. When l-α-triazopropionic acid is reduced with aluminium amalgam, d-alanine is formed.

229. "*The Triazo-group.* Part VI. *Triazoethyl Alcohol and Triazoacetaldehyde.*" By Martin Onslow Forster and Hans Eduard Fierz.

Triazoethyl alcohol (2-*triazoethanol*-1), $N_3 \cdot CH_2 \cdot CH_2 \cdot OH$, prepared from ethylene chlorohydrin and sodium azide, is a colourless, sweet-tasting, odourless liquid, having specific gravity 1·149 compared with water at 24°, and boiling at 60° under 8 mm. pressure; treatment with stannous chloride eliminates nitrogen, and produces aminoethyl alcohol. *Triazoethyl acetate*, $CH_3 \cdot CO_2 \cdot C_2H_4N_3$, has specific gravity 1·126 compared with water at 24°, and boils at 74° under 20 mm. pressure; the odour is much more pronounced than that of ethyl triazoacetate, resembling that of ethyl acetate in character and intensity.

Triazoethyl p-*nitrobenzoate*, $NO_2 \cdot C_6H_4 \cdot CO_2 \cdot C_2H_4N_3$, melts at 82°, and, on reduction with tin and hydrochloric acid, yields p-*aminobenzoyloxyethylamine*, $NH_2 \cdot C_6H_4 \cdot CO_2 \cdot C_2H_4 \cdot NH_2$, which melts at 78° when crystallised with $1H_2O$, the anhydrous base melting at 122·5°; the *picrate* and *dibenzoyl* derivative melt at 172—175° and 212° respectively.

Triazoacetaldehyde, $N_3 \cdot CH_2 \cdot CH{:}O$, obtained from chloroacetaldehyde hydrate and sodium azide, is an oil, which has not been purified on account of the readiness with which it undergoes change on heating, or when treated with various agents; its behaviour towards alkalis resembles that of the triazo-ketones.

230. "*Contribution to the Chemistry of the Cholesterol Group.* Part II. *Some Oxidation Products of Sitosterol.*" By Robert Howson Pickard and Joseph Yates.

The behaviour on oxidation of the vegetable cholesterol, sitosterol, has been studied. This alcohol, which is obtained from the fat contained in wheat, yields oxidation products which are analogous to those given by cholesterol itself.

Using a nomenclature similar to that of Windaus (*Arch. Pharm.*, 1908, [2], ccxlvi., 117) for cholesteryl derivatives, the following are the products obtained :—By the action of hydrogen peroxide on sitosterol, *dehydrositostanetriol*, $C_{27}H_{46}O_3$, m. p. 252°, and its *diacetate*, m. p. 138—139°; by the action of chromium trioxide on the triol, *dehydrositostanedionol*, $C_{27}H_{42}O_3$, m. p. 256°; by the action of dehydrating agents on the dionol *dehydrositostenedione*, $C_{27}H_{40}O_2$, m. p. 166°, and its *monophenylhydrazone*, m. p. 247°; by the action of zinc-dust on the unsaturated dione, *dehydrositostanedione*, $C_{27}H_{42}O_2$, m. p. 196°, and its *dioxime*, m. p. 187°; by the oxidation of the saturated dione with chromium trioxide, a *ketodicarboxylic acid*, $C_{27}H_{42}O_5$, m. p. 236°, and its *dimethyl* ester, m. p. 107°, and also the *oxime* of the ester, m. p. about 90°.

231. "*Experiments on the Synthesis of the Terepenes.* Part I. (cont.). *Resolution of* dl-1-*Methyl*-Δ¹-cyclo*hexene*-4-*carboxylic Acid and Synthesis of the Optically Active Modifications of Terpineol.*" By Kenneth Fisher and William Henry Perkin, jun.

The authors have synthesised *d*- and *l*-terpineol from the esters of the *d*- and *l*-modifications of 1-methyl-Δ¹-*cyclo*hexene-4-carboxylic acid, $CMe\begin{matrix}=CH-CH_2\\ -CH_2-CH_2\end{matrix}>CH \cdot CO_2H$, and have attempted to convert them into the optically active modifications of limonene.

232. "*Experiments on the Synthesis of the Terpenes.* Part XIII. *Synthesis of* iso*Carvestrene* (Δ6 : 8(9)-m-*methadiene*) *and its Derivatives.*" By Kenneth Fisher and William Henry Perkin, jun.

The authors have synthesised 1-*methyl*-Δ⁶-cyclo*hexene*-3-*carboxylic acid*, and have converted it into *dihydro*iso-*carvestrenol* (I.) and iso*carvestrene* (II.) :—

$$CH\begin{matrix}=CMe \cdot CH_2\\ -CH_2 \cdot CH_2\end{matrix}>CH \cdot CMe_2 \cdot OH$$

I.

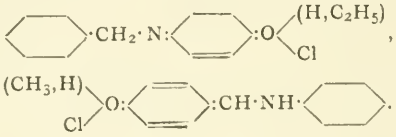
$$CH\begin{matrix}=CMe \cdot CH_2\\ -CH_2-CH_2\end{matrix}>CH \cdot CMe{:}CH_2.$$

II.

233. "*Colour and Constitution of Azomethine Compounds.*" (Part II.). By Frank George Pope and Robert Fleming.

The simplest hydroxyazomethine compounds and their ethers are colourless substances, but their hydrochlorides, which are formed by passing hydrogen chloride into benzene solutions of the azomethines, show absorption in

the blue and violet region of the visible spectrum. Consequently, it seems necessary to conclude that the salts formed by the action of mineral acids on the azomethines possess a different structure from the azomethines themselves, and it appears most rational to regard them as oxonium salts, thus:—

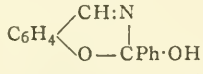


234. "*Aromatic Arsonic Acids.*" By MARMADUKE BARROWCLIFF, FRANK LEE PYMAN, and FREDERIC GEORGE PERCY REMFRY.

Sodium *bis*-2-aminotolyl-5-arsinate described by Pyman and Reynolds (*Trans.*, 1908, xciii., 1180) is of little use in trypanosomiasis. The authors have prepared several derivatives of *p*-aminophenylarsonic acid and 2-aminotolyl-5-arsonic acid for possible use in trypanosomiasis; their trypanocidal properties were found to be very slight.

235. "*The Condensation of Salicylaldehyde and Benzamide.*" By ARTHUR WALSH TITHERLEY and MORRIS EDGAR MARPLES.

The condensation of salicylaldehyde and benzamide in the presence of sodium acetate produces two isomeric *salicylidenebenzamides*, $HO\cdot C_6H_4\cdot CH:N\cdot CO\cdot C_6H_5$, and not the cyclic "coumarazine,"—



described by Cebrian (*Ber.*, 1898, xxxi., 1592). The two compounds, which are similar in properties and phenolic in character, were separated by means of acetone.

When condensation between salicylaldehyde and benzamide occurs in presence of hydrogen chloride, wandering of benzoyl occurs, and O-N-N-*tribenzoylsalicylidenediamine*, $BzO\cdot C_6H_4.CH(NHBz)_2$, m. p. 198°, is formed, which is hydrolysed by pyridine and alkali, forming ammonia, benzoic acid, salicylaldehyde, and dibenzamide. The production of the latter shows that a wandering of benzoyl takes place similar to that which occurs in the synthetic formation of the tribenzoyl derivative.

By cautious hydrolysis of the tribenzoyl derivative with cold aqueous alcoholic sodium hydroxide, one benzoyl group is eliminated with the production of N-N-*dibenzoylsalicylidenediamine*, $HO\cdot C_6H_4\cdot CH(NHBz)_2$, m. p. 192°.

236. "*The Coumarin Condensation.*" By ARTHUR CLAYTON.

A study has been made of the formation of coumarins from substituted phenols and malic acid or ethyl acetoacetate. The following conclusions are drawn:—

1. Phenols of the types shown in formulæ I. and II. (where X is an alkyl, hydroxyl, or dialkylamino group) condense readily with malic acid or ethyl acetoacetate to form derivatives of coumarin:—

2. Chlorine as a substituent has an effect similar to that of the above groups, but its influence is very much less marked.

3. The introduction of such substituents as NO_2, CO_2H, and $CO_2\cdot C_2H_5$ prevents condensation.

237. "*Experiments on the Synthesis of 1-Methylcyclohexylidene-4-acetic Acid.*" (Part II.). By VICTOR JOHN HARDING, WALTER NORMAN HAWORTH, and WILLIAM HENRY PERKIN, jun.

The authors bring forward evidence which, in their opinion, clearly proves that the acid of melting-point 41°, obtained by Marckwald and Meth (*Ber.*, 1906, xxxix., 1171) by the elimination of water from 4-hydroxy-1-methyl*cyclo*hexyl-4-acetic acid,—

$$CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C(OH)\cdot CH_2\cdot CO_2H,$$

is 1-methyl-Δ^3-*cyclo*hexene-4-acetic acid,—

$$CHMe<\begin{matrix}CH_2—CH\\CH_2\cdot CH_2\end{matrix}\geqslant C\cdot CH_2\cdot CO_2H,$$

and not, as the above investigators claim to have established, 1-methyl*cyclo*hexylidene-4-acetic acid,—

$$CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C:CH\cdot CO_2H.$$

PHYSICAL SOCIETY.

Ordinary Meeting, November 13th, 1908.

Dr. C. CHREE, F.R.S., President, in the Chair.

THE meeting was held, by kind invitation of Prof. F. T. Trouton, in the Physical Laboratory at University College.

Dr. FLEMING communicated a note on the "*Photo-electric Properties of Potassium-soaium Alloy*," illustrated by experiments.

The author said that, in connection with further researches on radio-telegraphic wave-detectors of the oscillation valve type, he had been led to examine instances of electronic emission other than those due to the incandescence of metals or carbon, to ascertain how far rectifying effects with high frequency currents could be obtained by them. It is well known that under the action of ordinary and ultra-violet light the electro-positive metals lose a negative charge of electricity, the effect being most pronounced in the case of rubidium, potassium, and the liquid alloy of potassium-sodium.

Dr. Fleming described a mode of making a tube in which potassium and sodium could be melted together and then decanted over into a chamber containing a platinum plate, so that a mass of the liquid potassium-sodium alloy having a perfectly clean surface, and the platinum plate fixed above it in an inclined position, could be constructed. By means of platinum wires sealed through the glass tube, a contact is made respectively with the platinum plate and the liquid alloy. When the surface of the alloy is illuminated by a powerful beam of light and the galvanometer connected to the platinum plate and alloy, it is found that a current is produced in this circuit merely by the action of the light, and by balancing this current against a variable electromotive force it was shown that an electromotive force varying from 0·4 to 0·8 of a volt is produced in the photo-electric cell due to the action of the light.

It was then shown that this photo-electric effect was greatly dependent an the colour of the light, and especially upon light absorbed by the alloy. The most effective rays in the case of potassium-sodium alloy having in it some excess of potassium, are the violet rays which can pass through cobalt glass, but even a very thin sheet of yellow glass cuts off the effect entirely. Elster and Geitel's experiment was then shown illustrating the effect of the plane of polarisation of the incident light. A powerful beam of light polarised by a Nicol prism was thrown upon the alloy's surface, and the self-produced photoelectromotive force was shown to be a maximum when the plane of polarisation of the beam was perpendicular to the plane of incidence of the light, thus showing that a maximum effect of the light is produced when the electric vector in the ray is perpendicular to the surface of the alloy, but a minimum when it is at right angles.

It was then shown that the photo-electric effect is greatly diminished by making even a feeble magnetic field parallel to the surface of the alloy. By the use of two such cells placed in series, Dr. Fleming showed that the photo-

electromotive force of each were additive, and indicated the possibility of making a battery of high voltage by the action of light upon a rubidium surface. Such a cell has more or less unilateral conductivity, and can therefore be used to rectify high frequency currents, but the effect is inferior to that produced by the author's oscillation valves, particularly by his latest type of valve.

Some questions were then discussed tending to show that the source of the photo-electromotive force cannot be identical with the volta-contact electromotive force in the circuit, but is due to the absorption of light by the sensitive surface. In all cases of such photo-electric action, the rays which are effective in producing it are those given out by the substance if heated or otherwise made radiant. Thus, zinc is photo-electric under the action of ultra-violet light, and ultra-violet light is largely radiated when an electric spark is taken between the zinc balls, or an electric arc between zinc poles. The photo-electric effects in the case of potassium are probably due to the absorption of the violet ray emitted by potassium when heated.

Some points of interest in connection with radio-telegraphy were then discussed. It has been shown that perfectly dust-free air is not ionised by ultra-violet light. If therefore the absorption of radio-telegraphic electric waves, which is found to exist when they pass through long distances of sunlit air, is due to the presence of free ions in the air, this may arise from the photo-electric action of the light upon dust particles. This suggests the question whether these particles may not be the same which create the blue colour of the sky, and if these particles absorb ultra-violet light, and thereby create ionisation, that would account for the relatively small percentage of ultra-violet light found in sunlight at the earth's surface, and also suggests the need for further observations on the principle of ions present in the atmosphere at various heights.

Prof. S. P. THOMPSON asked the author whether sodium was more sensitive to yellow light than to light of other wave-lengths,

Dr. R. S. WILLOWS remarked that the E.M.F. was in the direction required by theory: the alloy emits negative ions, and hence the direction of flow of negative electricity in the cell is from the alloy to the platinum, or the alloy is the positive pole. The action was similar in results to those produced by solution pressure when metals were immersed in acids except that the ions produced by light were of the other sign. Prof. Fleming's idea that metals respond to those rays only which they absorb was interesting in view of the fact that the weight of evidence was in favour of the emission of ions being due to an explosion in the atom arising from resonance, but Ladenburg's experiments did not support Dr. Fleming's theory. He measured the intensity of the light with a thermo-couple, and found for the same intensity that the shorter the wave-length the more efficient was the light in producing emission of ions.

Dr. FLEMING, in reply to Prof. Thompson, said sodium was most sensitive to yellow light.

A paper entitled "*Electric Splashes on Photographic Plates*" was read by Mr. ALFRED W. PORTER.

The author showed by means of transparencies the effect of a normal magnetic field upon the patterns which appear in developing a photographic plate which is placed between two terminals between which a sudden discharge passes. This effect is confined to the main line of discharge, and consists in this line being broadened into a band of nearly constant width; a very similar result is obtained if a blast of air sweeps across the plate instead of the magnetic field being employed. This broad band is produced by the glowing gas which surrounds the spark itself. The palm-like figures and the ramifications leading up to them do not seem to be modified by the magnetic field; and the author concludes that these figures are therefore determined by events independent of the *motion* of the changes conveyed along them, or else that the moving charges have a very large mass associated with them. In the course of the experiments the author found that in different gases at atmospheric pressure the figures obtained when the *negative* terminal is on the sensitive side of the plate are very different one from another. In air they suggest palm leaves, in carbonic dioxide they are much more feather-like, while in oxygen the ramifications are much more curvilinear than in air which forms lines which change their directions very abruptly; again, in coal-gas the figures resemble tap-roots of plants. When the positive terminal is above the plate the figures are nearly the same in all these gases; a result which is contrary to the results obtained at low pressure in vacuum-tubes. A series of transparencies was also shown showing the effects obtained in air at various pressures; very marked changes are obtained as the pressure is reduced from 76 to 10 cm.

Prof. F. T. TROUTON said the author's experiments were upon a subject which had been neglected, and might lead to fruitful results. There were a number of details visible on the plates themselves which did not show up upon the screen. It was necessary to simplify the conditions of the experiments as much as possible.

Prof. S. P. THOMPSON said the experiments opened up a fertile field of inquiry. Variations of the experiments might be tried and important results obtained. The nature of the film used obviously had something to do with the pattern produced.

Mr. A. W. PORTER, referring to Prof. Thompson's remarks, said that the figures obtained did not seem to depend upon the nature of the photographic plates used. The surrounding gas seemed to be mainly responsible for the kind of patterns produced.

Mr. ALFRED W. PORTER showed an experiment on an Anomaly in the Lagging of Thin Wires and Narrow Pipes

When thin wires and narrow pipes are covered with a lagging material it is not possible at once to say whether the covering will keep heat in or assist it to escape. There is a critical radius equal to the ratio of the conductivity of the material to the emissivity from its surface which the outer covering must exceed before it begins to act as a lagger. Although this seems to have been recognised by Prof. Bottomley and others, the results of experiments which have previously been made would seem to indicate that the effect in practice is very small indeed. The author showed a simple lecture experiment in which a large effect is obtained. A thin platinum wire (0·2 mm. radius) is coated at intervals along its length with glass of about 2 mm. outer radius. When an electric current is passed through the wire of sufficient strength to raise the uncoated portions to (say) 800° C., the coated portions do not even glow, and measurements have shown that they remain at about 100° C.; there is thus a difference of about 700° on the wrong side. A thickness of coating can be obtained which is such as to allow the same escape of heat as from a practically uncoated wire. To illustrated this, two narrow steam-pipes were shown—one coated with a single layer of asbestos paper, the other with a very thick coat. The two were equivalent in their power of preventing escape of heat. An intermediate thickness of coat would have made a *worse-lagged* pipe than either of them.

A paper "*On the Rate of Growth of Viscosity in Congealing Solutions*" was read by A. O. RANKINE, B.Sc.

The author exhibited apparatus and described experiments for the determination of the time variation at constant temperature of the viscosity of gelatin solutions of high concentration. These solutions, if quiescent, after a time possess rigidity, but continual stirring prevents its appearance and the solution remains liquid. The method of measurement, which consisted in measuring the couple on an inner cylinder when an outer concentric cylinder was rotated (the interspace being filled with the solution), secured this condition. The simple law $\eta = a - be^{-\lambda t}$ was found to hold very accurately for values of the time not too small. The values of the constants a, b, and λ are,

however, very dependent upon the temperature at which the solution is kept. On carrying the measurements to lower temperatures, it was found that a sudden rapid rise of viscosity occurred at times and in a manner over which control has not yet been obtained. It was suggested that this was analogous to the case of ordinary supersaturation. Further experiments are to be made on this point.

Dr. A. Griffiths expressed his interest in the experiments, and asked if the vigour of the stirring employed was connected in any way with the sudden change in the viscosity.

Prof. C. H. Lees pointed out that the author was not measuring the viscosity of a homogeneous liquid, but of a liquid in which lumps of gelatin were present. The sudden jump in the curve was due to a particular arrangement of these lumps.

Mr. A. O. Rankine said the rate of stirring was the same in all experiments, namely, just under two revolutions per second.

Prof. F. T. Trouton described the construction of curves to exhibit the relations which must subsist between the concentration and temperature of a solution in order that the same weight of the solute may be adsorbed per square centimetre on introducing a solid on which adsorption takes place. To such a curve the name of *isonere* has been given. When the isoneres for different weights adsorbed are compared, it is found that they consist of similar curves—that is to say, for any two isoneres the ratio of the concentration ordinates is the same for all temperatures. In addition, it is found that the saturation curve for the solution, or that showing the maximum concentration possible at each temperature, is also similar to the isoneres. Thermodynamic considerations lead to the former result provided we suppose that the latent heat of adsorption is constant for different concentrations, and to the latter if the latent heat of solution at saturation is of the same value as that of adsorption.

A paper entitled "*Note on the Recombination of Ions in Air*" was read by Dr. Phillips.

NOTICES OF BOOKS.

Komprimierte und Verflüssigte Gase. ("Compressed and Liquefied Gases"). By Dr. H. Teichmann. Halle-a-S: Wilhelm Knapp. 1908.

The use of compressed and liquefied gases commercially has during recent years been greatly extended, and a text-book dealing shortly with the subject will be welcomed. Although a gas was liquefied for the first time nearly a hundred years ago, the application of the method then adopted, and subsequently modified and improved, for the purpose of putting pure gases upon the market in a convenient form, has been the work of at most the last thirty years. Thus the author has not had to report many comparatively trifling changes in procedure and apparatus, but, on the other hand, has sometimes occasion to call attention to defects and prophesy improvements. The gas laws of Charles and Boyle are first discussed in an introductory section, and the author then passes on to the mechanical means adopted for compression, and describes the different types of compressors. The methods of preparing certain gases are next treated. In choosing the gases for consideration the author has been guided partly by their technical importance; in addition he has endeavoured to select only those which are liquefied by typical methods—passing over others for which special and very often more or less secret processes are employed. The construction of containers for compressed and liquefied gases is treated in one chapter, and the regulations in force in Germany concerning their transport and storage are also included.

Report of Recent Advances in Pharmaceutical Chemistry and Therapeutics. Vol. XXI. Darmstadt: E. Merck. 1908.

This annual report, which is sent free on application to doctors and others interested in pharmacy, gives an impartial account of advances in pharmaceutical chemistry which have been made during the year 1907. Not only are new therapeutical preparations which have come into use during the year described, but also the applications of well known drugs for fresh purposes are chronicled. Thus the book really constitutes an abstract of the pharmacopœia, and doctors will appreciate the assistance it gives them in prescribing as well as the valuable references to periodical literature.

MISCELLANEOUS.

Royal Society of Arts.—The opening meeting of the one hundred and fifty-fifth session of the Royal Society of Arts was held on Wednesday evening, the 18th inst., when an address was delivered by Sir William H. White, K.C.B., LL.D., F.R.S., Vice-President and Chairman of the Council. The following papers will be read at the ordinary meetings before Christmas:—November 25, Sir W. Martin Conway, M.A., F.S.A., F.R.G.S., "The Goldfields of Eastern Peru and Bolivia"; December 2, Eric Stuart Bruce, M.A., "Mechanical Flight"; December 9, G. Albert Smith, F.R.A.S., and Charles Urban, F.Z.S., "Kinematography in Natural Colours"; December 16, Primrose McConnell, B.Sc., F.C.S., "London Milk Supply from a Farmer's Point of View." A paper by Douglas Dewar, I.C.S., on "The Birds of India," will also be read before the Indian Section of the Society on the 10th December. There will be one course of Cantor Lectures before Christmas by Oscar Guttmann, M.Inst.C.E., F.I.C., F.C.S., on "Twenty Years Progress in Explosives." The course consists of four lectures, delivered on November 23, 30, and December 7, 14.

MEETINGS FOR THE WEEK.

Friday, 27th.—Physical, 5. "Graphic Method of dealing with Refracting Surfaces," by H. S. Allen. "Method of Determining Moments of Inertia," by (the late) W. Cassie. "Experimental Examination of Willard Gibbs's Theory of Surface Condensation regarded as the Basis of Adsorption," by W. C. M. Lewis. "Diffusion of Actinium and Thorium Emanations," by S. Russ. "Elliptic Polarisation produced by the Direct Transmission of a Plane Polarised Stream through a Plate of Quartz cut in a Direction Oblique to the Optic Axis, with a Method of Determining the Error of a Plate supposed to be perpendicular to the Axis," by J. Walker.

Monday, 30th.—Royal Society of Arts, 8. (Cantor Lecture). "Twenty Years Progress in Explosives," by O. Guttmann.

Wednesday, Dec. 2nd. Royal Society of Arts, 8. "Mechanical Flight," by E. S. Bruce.

—— Society of Public Analysts, 8. "Gravimetric Estimation of Antimony and Tin," by E. Cahen and G. T. Morgan. "Oil from *Carapa Guianensis*," by J. Lewkowitsch. "Detection and Estimation of Formaldehyde in Milk," by H. S. Shrewsbury and A. W. Knapp. "Determination of Aldehydes in Oil of Lemon," by A. H. Bennett. "Some Analyses of Cream Cheese," by C. H. Cribb.

Thursday, 3rd.—Chemical, 8.30. "Double Salts of Potassium Iodide with Mercury Iodide and Camphor Dimercuriodide in Organic Solvents," "Action of Mercuric Iodide on Ketones in Alkaline Solution," and "Condensation of Camphor with Mercuric Iodide," by J. E. Marsh and R. de J. Fleming-Struthers. "Relation between Absorption Spectra and Chemical Constitution — Part XIII., Some Pyrones and Allied Compounds," by E. C. C. Baly, J. N. Collie, and H. E. Watson. "Organic Derivatives of Arsenic—Part I., Dicamphoryl-arsinic Acid," by G. T. Morgan and Miss F. M. G. Micklethwait. "Tellurium Dicyanide" and "Boron Thiocyanate," by H. E. Cocksedge.

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THE PRESENT STATE OF OUR KNOWLEDGE OF RADIO-ACTIVITY.*

By A. DEBIERNE.

Part II.—*The Transformations of Radio-active Substances.*

In the first part of this article (*Revue Générale des Sciences*, Sept. 15, 1908, xix., p. 691; Chemical News, xcviii., 235 *et seq.*) we showed that four series of radio-active transformations are known. We have seen that the sequence of the different terms of each series is not a result obtained by theoretical reasoning; it is an experimental fact which has been thoroughly established in most cases.

In the modern theory of these transformations which has been worked up by Rutherford and Soddy, and which is based upon the hypothesis of atomic transmutation formerly enunciated by Pierre Curie and Mdme. Curie, each term represents a distinct chemical element which is distinguished from the ordinary chemical elements only by its short life and by the emission of a special radiation. The disappearance of the radio-active atom is the result of its transformation into another atom. The special radiation is a form of energy which accompanies this transformation. According to this theory the study of radio-activity has already led to the discovery of about twenty new elements.

However, if the chemical individuality of the heads of the series—uranium, thorium, radium—is indisputably proved by the atomic weights and the characteristic spectra, and if by analogy it may be expected that the same thing will be proved in the case of actinium, for all the other terms, as we have seen, although certain characteristics of a chemical or physical order have been observed, which enable us to distinguish and separate them (as ordinary chemical elements are separated), yet it cannot be said that these characteristics definitely prove the existence of new chemical elements. And it would not be absurd to suppose that the radio-active properties observed are due to special centres of energy which attach themselves to ordinary matter, just as electric charges or electrons attach themselves to atoms, sometimes profoundly modifying their properties, and which undergo the successive transformations. (*Cf.* the case of aqueous solutions in which the molecules are dissociated into ions). As a matter of fact, up to the present it has not been directly proved that one of the radio-active transformations previously described has ended in the disappearance of an atom, characterised by a spectrum and an atomic weight, and the appearance of a new atom characterised by a new spectrum and a new atomic weight. Even if the theory is perfectly correct this proof would be exceedingly difficult to establish, for the quantity of matter transformed in an interval of time available for experiments would be very small.

However, a certain number of facts are known which agree perfectly with the theory of an atomic transmutation; and if these facts do not directly verify the details of the above mentioned transformations they may be regarded as forming a solid experimental basis for all the theories which assume the occurrence of transformations of the atom in the phenomena of radio-activity.

I.

I shall first discuss experiments which show that radio-active substances continuously produce the gas helium. The discovery of this important fact is due to Ramsay and Soddy, who observed it with the compounds of radium.

* *Revue Générale des Sciences* 1908, xix., 730.

Giesel had discovered that radium salts decompose water into oxygen and hydrogen, and that a solution of radium continuously sets free detonating gas. Ramsay and Soddy proved in their first experiments that the gas set free by a solution of a radium salt contains a small quantity of helium. They also showed that helium is produced when radium emanation is separated by condensation in liquid air, and when this emanation is allowed to decay spontaneously. The formation of helium by radium salts is an undoubted fact. It has since been established by a great number of experimenters, including Pierre Curie and myself.

The experimental method I employed is a little different from that used by Ramsay. It consists in introducing the gases set free in a solution of radium into a tube containing different substances which absorb hydrogen, oxygen, nitrogen, and the oxides of carbon, and leave only the gases of the argon family. The gaseous residue is then driven back by means of mercury into a very fine capillary tube. A special arrangement enables the gas to be divided into two equal parts; one part is used for the spectroscopic examination, while the other is exposed to atmospheric pressure, when it forms a little bubble of gas in a capillary tube between two columns of mercury; the volume of this bubble can be determined fairly accurately. This volume is of the order of a tenth of a cubic millimetre. The spectroscopic examination showed that the helium gas is very pure. I have been able to carry out at intervals during are year a series ot experiments on the same radium solution, and have thus proved that the production of helium is continuous and proportional to the time. I have also shown that the compounds of actinium exhibit the same property, and also produce helium continuously in quantities which are proportional to the time of accumulation. (The amount of helium obtained with one of my products rich in actinium was equal to that produced by about 1 centigrm. of pure radium bromide). This fact has recently been confirmed by Giesel.

Using the property of radium emanation of condensing at the temperature of liquid air, Ramsay succeeded in obtaining the emanation in a very concentrated state. He proved that it then possesses a characteristic spectrum, that it follows the ordinary laws of compression of gases, and that it gives rise to the production of helium. Finally, he showed that the volume occupied by the emanation diminishes as a function of the time. Some years ago I performed some experiments dealing with this subject, and if I did not confirm all the results stated by Ramsay and his collaborators, I did observe this diminution of volume ot the emanation, which in my experiments was under atmospheric pressure. I observed that at the end of a few days the volume had become very small, being reduced to about one-twentieth of its original value. I must mention that the results of different experiments performed with the emanation do not agree very well; moreover, the experiments are very delicate, and altogether a more profound study of the question is very necessary.

The principal result of all these experiments is that radium and actinium continually produce helium, and that the production of helium is connected with the presence of active substances. I have performed many confirmatory experiments, and I have never proved the formation of helium except in presence of these substances.

The formation of helium cannot be explained in a reasonable manner, except by assuming the occurrence of an atomic transmutation.

Another very important result is due to Pierre Curie and Laborde, who measured the quantity of energy set free in radio-active transformations. The result showed that an enormous amount of energy is liberated in the phenomena of radio-activity. A grm. of radium in equilibrium with its transformation products sets free more than 100 calories per hour; *i.e.*, about 1,000,000 calories in a year. In this period of time the fraction of radium transformed can only be very small. We shall see presently that the mean duration of life of radium can be calculated upon the basis

of certain hypotheses; it would be about 3000 years. Then the total energy of transformation of 1 grm. of radium would be three thousand million calories, a quantity equivalent to that disengaged by the combustion of several tons of carbon.

The phenomenon of the liberation of heat is very easy to prove when a sufficient quantity of radium is used. It may be observed qualitatively as follows:—Two identical Dewar flasks are placed in the same receptacle in which the temperature is uniform. A tube containing radium is introduced into one of these flasks, and in the other is placed a tube containing an inactive product. A sensitive thermometer is placed in each flask. A difference of temperature between the two flasks can then be detected, that containing the radium having a temperature which is higher by some degrees. Measurements have been made with a calorimeter, and thus the result stated above has been obtained. With actinium salts I have been able to demonstrate a disengagement of heat sufficient to give a difference of some tenths of a degree between two Dewar flasks, in an experiment like that just described.

It has been shown that energy is set free in all the successive transformations which radium undergoes, and there is reason for thinking that a large part of this energy is due to the kinetic energy of the α-particles.

Whatever theories of the constitution of matter are adopted the atom must be regarded as an extremely stable system which has hitherto resisted all external agents; then it is natural to suppose that the transformation of such a stable structure would set free a much larger amount of energy than the transformation of a molecule. The production of an enormous quantity of energy in the phenomenon of radio-activity must thus be regarded as a weighty argument in favour of an atomic transformation. The fact that the energy produced is divided between the different stages of the radio-active transformations is also an argument in favour of the existence of different intermediate atoms.

The conception of an atomic transformation being agreed to, the nature of this transformation must be defined in each case.

The first condition is imposed by the laws of the transformation; it must be monatomic; that is, only one atom must be implicated at a time. (It may, however, take place between two atoms if the concentration of one is very great and practically constant). It follows that the new atoms produced can only have a mass equal or inferior to the mass of the first; the laws are unaltered when the result of the transformation is the production of several new atoms. It is difficult to imagine that the transformation of an atom lasts an appreciable time, and it is generally supposed that the transformation is instantaneous and analogous to an explosion. The different atoms which form a certain mass of matter are successively transformed with a frequency which depends upon their nature.

The production of a special radiation, which consists in a projection of particles of different kinds, agrees equally well with the hypothesis of an explosion.

Very definite hypotheses concerning the nature of the transformation have been formulated by Rutherford. In the first place when a radio-active atom is transformed only one new radio-active atom is produced. For instance, one atom of radium which gives one atom of emanation gives one atom of radium A, &c. To explain the formation of helium, Rutherford and Soddy have supposed that the α-rays are formed by the projection of positively charged helium atoms. To make this hypothesis agree with the value of e/m for the α-rays, Rutherford has assumed that the charge e is double the charge on an element in electrical phenomena. He has also supposed that in each transformation with α-rays only one α-particle is emitted; that is, only one helium atom for each radio-active atom which undergoes transformation. When the transformation takes place without the emission of α-rays the mass of the atom does not undergo any variation in the transformation. Hence it follows that the different terms of a series must have atomic weights which do not differ much from one another.

The atomic weight of radium being 226·5, that of the emanation will be 224·5, that of radium A 218·5, radium B 214·5, radium C 214·5, since radium B does not emit α-rays, radium D 210·5, radium E 210·5, radium F 210·5, and the last unknown term 206·5.

This last atomic weight, which is very nearly that of lead, led Rutherford and Boltwood to suppose that the result of the transmutation of radium is lead. Boltwood has endeavoured to support this view by instancing the lead contained in radio-active minerals; but according to more recent researches it appears that some radium minerals do not contain lead. The formation of lead from radium is thus as yet purely hypothetical.

The results of experimental determinations of the atomic weights of the gaseous emanations do not agree with the numbers given above.

We know that the coefficient of diffusion of a gas is approximately inversely proportional to the square root of its molecular weight. The concentration of an emanation being easily determined relatively, it is possible to determine the coefficients of diffusion of the different emanations in different gases.

The measurements are not very accurate for the emanations of thorium and radium, but the numbers point to a molecular weight equal to about 100. With actinium I have been able to get an accurate result, and have found that the molecular weight is 70.

If it is supposed that the emanations are monatomic gases of the argon family, which is in agreement with the fact that they cannot be made to enter into combination, the molecular weight is the same as the atomic weight, whereas the number is at least twice as small as that given by the above theory. (If the emanations were diatomic the atomic weights would be twice as small again). These numbers, obtained by diffusion experiments, are founded upon an experimental basis which seems to be correct, and I think that there is reason for believing that in the transformation of an atom of radium two atoms of emanation are formed. This makes no change in the law of transformation. It also seems possible that phenomena of agglomeration occur in the other terms of the series. This agglomeration might have no influence on the true laws of radio-active transformations.

In all theories of atomic transmutation we are led to the conclusion that the active substances disappear gradually with the time. This phenomenon must therefore occur with the heads of the series uranium, thorium, radium, and actinium. No disappearance has been proved directly by experiment; this shows at any rate that only a very small fraction of the total mass is transformed at the end of several years. Nevertheless, attempts have been made to calculate indirectly the hypothetical law of decay and the mean duration of life of these active substances. Some of the above hypotheses are used in the calculation.

Rutherford based one of his calculations on the magnitude of the positive charge expelled in the form of α-particles.

By assuming that only one α-particle is expelled when a radium atom disappears, and that this particle has an electric charge equal to twice the charge on an element, and by determining experimentally the electric charge expelled in a given time for a known quantity of radium, the data are obtained for calculating the proportion of atoms which disappears per second and the mean duration of life of a radium atom. A similar but less direct calculation has been made for uranium and thorium.

Moreover, in different experiments Ramsay has obtained the emanation in a very concentrated state, and has measured the volume of emanation produced in a given time. Adopting the hypothesis that an atom of emanation is produced by the disappearance of an atom of radium, the mean duration of life of radium can also be calculated. This period could also be obtained by observing the volume of helium yielded, employing the above hypotheses on the formation of helium.

The numbers thus obtained, based on hypotheses which have not yet been established, and upon experiments which are by no means accurate, vary within fairly wide limits. The mean duration of life would be between 250 and 3000 years, that of uranium would be of the order of 5×10^9 years, and that of thorium of 10^{10} years.

(To be continued).

ON HIGH TENSION BRONZES.

By SERGIUS KERN, M.E., St. Petersburg.

HIGH tension bronzes—as, for instance, manganese bronze—deserve more attention than they usually receive from engineers. Apart from their physical qualities (tensile strength and elongation), which come near to those of steel castings, and the keeping of these qualities with small diminution at temperatures of high-pressure marine boilers (which the ordinary gun-metal fails to do), the high tension bronzes, containing about 60 per cent copper, 38 per cent zinc, and certain quantities of iron and manganese, have none or only small quantities of tin. This metal may be considered a speciality for liquation processes.

Such a nuisance as liquation we often observe in gun-metal castings for different fittings (valves, &c.) for high-pressure boilers. This is a great evil, as it gives rise to a heavy loss in ready machined fittings, which before delivery must stand serious and heavy hydraulic testing (very often 600 lbs. to the square inch). The cause of failures is chiefly due to liquation effects, which were not so harmful when small pressures in testing were applied (say, 90 lbs. per square inch), when marine boilers worked at low pressures. At those times gun-metal castings satisfied the demands of engineers.

Some years ago we made many trials and witnessed many experiments with Parsons' manganese bronze, and what struck us was the absence of liquation, speaking practically, in high tension bronzes, and that is the reason why we always insisted that such bronzes, apart from their physical qualities, must be more widely used instead of the old gun-metal.

In conclusion, we may add that small defects in high-tension bronzes when tried under hydraulic pressure, may be easily and safely chased by hammering. Such a method for gun-metal castings is out of the question.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

PART III.—ANALYSIS OF THE ALUMINIUM AND IRON GROUPS, INCLUDING BERYLLIUM, URANIUM, VANADIUM, TITANIUM, ZIRCONIUM, AND THALLIUM.

By ARTHUR A. NOYES, WILLIAM C. BRAY, and ELLWOOD B. SPEAR.

(Continued from p. 265).

Confirmatory Experiments and References (continued).

Solubility of Uranyl Vanadate in Sodium Hydrogen Carbonate Solutions.—Solutions containing 100 mgrms. U as $UO_2(NO_3)_2$ and 60 mgrms. V as Na_3VO_4 were mixed, a few drops HNO_3 (1·20) were added to dissolve the precipitate, the mixture was diluted to 100 cc., 2 grms. $NaHCO_3$ were added, and the mixture was digested in a closed bottle at 95° for half an hour; no precipitate separated. The mixture was cooled down, 40 mgrms. V as Na_3VO_4 were added, making 100 mgrms. in all, and the mixture was again heated at 95° for half an hour; no precipitate separated in the hot solution, nor in the cold on standing several days. The experiment was repeated with 100 mgrms. U and 100 mgrms. V, except that the mixture was first treated with NaOH and H_2O_2 by P. 52, and that 1·5 grms. $NaHCO_3$ were used instead of 2 grms.; the result was nearly the same. 100 mgrms. U as $UO_2(NO_3)_2$, 100 mgrms. V as Na_3VO_4, and 3 grms. $NaNO_3$ were treated by *P. 58*a*, 1 grm. excess of $NaHCO_3$ being added; a precipitate formed on adding $NaHCO_3$, and a considerable one remained after heating the mixture at 100° in a closed bottle for thirty minutes. The precipitate and filtrate were analysed for uranium and vanadium by *P. 58*c*—*e*: the filtrate was found to contain 35 to 40 mgrms. of uranium, and all but 10 or 15 mgrms. of the vanadium.

The last experiment was repeated except that the mixture was warmed in a flask at 95° (without allowing it to boil) for thirty minutes; the precipitate that remained was smaller, and contained only 10 to 20 mgrms. U and 2 to 5 mgrms. V. The last experiment was repeated except that the mixture was boiled for one minute in an open flask; the precipitate dissolved completely, and no precipitate formed on cooling even in twenty-four hours, showing that uranyl vanadate is more soluble in slightly alkaline carbonate solutions than in those from which the CO_2 is prevented from escaping.

An acid solution containing 50 mgrms. V as Na_3VO_4, and 50 mgrms. U as $UO_2(NO_3)_2$ was diluted to 100 cc. and neutralised by adding a little powdered $NaHCO_3$. Then 0·5 grm. $NaHCO_3$ was added, and the mixture was heated in a pressure bottle at 95° for half an hour; on heating a large precipitate remained. To a solution containing 100 mgrms. V as Na_3VO_4, 20 mgrms. U as $UO_2(NO_3)_2$ and a known excess of HNO_3 (1·20) in 50 cc. (instead of 100 cc.) was added just sufficient $NaHCO_3$ to leave 1 grm. undecomposed $NaHCO_3$. The mixture was heated in a closed bottle at 95° for half an hour; no precipitate separated. To this solution after cooling, was added 20 mgrms. more U and the mixture was again heated at 95°; a large precipitate separated in the cold and remained on heating. The experiment was repeated with 100 mgrms. U and 10 mgrms. V: no precipitate separated. 10 mgrms. more V were added and the heating repeated; a large precipitate separated in the cold and remained on heating. The last experiment was repeated with 100 mgrms. V and 100 mgrms. U, and the precipitate and filtrate were analysed for uranium and vanadium by *P. 58*c* to *e*; the filtrate was found to contain 20 or 30 mgrms. of uranium and all but a few mgrms. of the vanadium.

Non-Precipitation of Uranyl Chromate, Phosphate, and Oxalate in the $NaHCO_3$ *Procedure.*—To a solution containing 100 mgrms. U as $UO_2(NO_3)_2$ 200 mgrms. Cr as K_2CrO_4, and a known (small) amount of HNO_3 (1·20) in 100 cc. was added enough $NaHCO_3$ to leave 1 grm. of the undecomposed carbonate; the mixture was heated in a closed bottle at 95° for half an hour; no precipitate separated. A solution containing 100 mgrms. U as $UO_2(NO_3)_2$ and 100 mgrms. PO_4 as $NaHPO_4$ was treated by P. 52 and then by *P. 58*a*; no precipitate separated in the $NaHCO_3$ procedure. After cooling an additional 250 mgrms. portion of PO_4 was added, and the heating repeated; no precipitate separated. The experiment was repeated with 100 mgrms. V as Na_3VO_4 and 200 mgrms. oxalic acid; no precipitate separated.

*P. 58*a*, N. 4: *Precipitation of Aluminium, Zinc, and Beryllium in Hot Sodium Hydrogen Carbonate Solutions in Open Flasks.*—2 mgrms. Al as nitrate and 3 grms. $NaNO_3$ were dissolved in 100 cc. water; a little $NaHCO_3$ was added until the mixture after shaking just ceased to react acid to litmus-paper; 1 grm. more was added; the mixture was heated to about 90°, and digested at this temperature in a covered flask on a water-bath for half an hour; the precipitate slowly dissolved, except a few small flakes

* From the *Journal of the American Chemical Society*, XXX., No.4.

The mixture was filtered while hot, and the filtrate tested for aluminium by acidifying with acetic acid, adding Na_2HPO_4 and heating to boiling; almost all the aluminium was found in the filtrate. This experiment was repeated twice with 2 mgrms. and with 1 mgrm.; the results were the same. The experiment was repeated twice with 20 mgrms. Al; the filtrate contained less than 1 mgrm. Al.

The experiments with 2 and 20 mgrms. were repeated, except that CO_2 gas was passed through the mixture; the results were nearly the same, except that the filtrate may have contained somewhat more aluminium, showing that there is no advantage in using CO_2 gas.

The experiment with 20 mgrms. Al was repeated except that the mixture was boiled for one minute; the filtrate contained 3 or 4 mgrms. Al. The experiment was repeated except that the mixture was allowed to cool before filtering; the filtrate contained about 1 mgrm. Al. The experiment was repeated with 4 mgrms. Al; the precipitate disappeared completely on boiling, but a precipitate separated out on cooling. The experiment was repeated with 6 mgrms. Al; a very small precipitate remained on boiling one minute.

1 mgrm. Zn as nitrate and 2 grms. $NaNO_3$ were dissolved in 100 cc., 1 grm. excess $NaHCO_3$ was added, and the mixture boiled in a flask for one minute; the precipitate did not dissolve and was proved to contain zinc by P. 53—57. The experiment was repeated with 20 mgrms. Zn; the filtrate being tested for zinc by acidifying with HNO_3, boiling, adding NH_4OH, and passing in H_2S; no precipitate formed, showing that the zinc was completely precipitated.

10 mgrms. Be as chloride and 2 grms. $NaNO_3$ were dissolved in 100 cc. water, $NaHCO_3$ was added until the mixture after shaking just ceased to react acid to litmus-paper; 1 grm. more was added; the mixture was boiled for one minute, and filtered while hot; the filtrate was acidified with HNO_3, evaporated to about 15 cc., and tested for beryllium by adding NH_4OH; the filtrate contained only about 0·1 mgrm. Be. The experiment was repeated except that the mixture was allowed to cool before filtering; the filtrate contained about 0·3 mgrm. Be. The experiment was repeated with 1 mgrm. Be; the precipitate remained on boiling for one minute, and did not disappear on standing in the cold for several hours.

These experiments were repeated with solutions containing from 1·5 to 5 grms. $NaHCO_3$ in 100 cc. of solution and varying quantities of beryllium; in a 1·5 per cent $NaHCO_3$ with 1 mgrm. Be little or no precipitate remained on boiling one minute; in a 2 per cent solution no precipitate remained with 2 mgrms. Be, but one remained with 4 mgrms.; in a 3 per cent solution 40 mgrms. Be dissolved almost completely, but 50 mgrms. gave a large precipitate. A comparison of these results with those obtained in a similar series of experiments in closed bottles (C. E., N. 3, above) shows that considerably more beryllium dissolves in concentrated $NaHCO_3$ solutions when the CO_2 is allowed to escape.

*P. 58*a*, N. 5: *Precipitation of Uranium with Aluminium or Beryllium in Hot Dilute Sodium Hydrogen Carbonate Solutions.*—See T. A., No. 171 to 175. In an analysis with 200 mgrms. Al and 10 mgrms. U, starting at *P. 58*a*, 1 or 2 mgrms. U were found in *P. 58*c*—*d*.

*P. 58*a*, N. 6: *Dissociation Relations of Carbonic Acid.*—See McCoy (*Am. Chem. Journ.*, 1903, xxix., 437).

Dissociation Relations of Chromic Acid.—See Spitalsky (*Zeit. Anorg. Chem.*, 1907, liv., 265) and Sherrill (*Journ. Am. Chem. Soc.*, 1907, xxix., 1641). The work of the latter shows that H_2CrO_4 dissociates in steps, first into HCr_4O^- and then into $CrO_4^=$, that the $HCrO_4^-$ is a very weak acid, and that the latter even in dilute solution is converted by dehydration in large measure, but by no means wholly, into dichromate-ion ($Cr_2O_7^=$).

(To be continued).

ON SCANDIUM.*

By Sir WILLIAM CROOKES, D.Sc., F.R.S.

SCANDIA is one of the rarest and least known of the recognised rare earths. It was discovered in 1879 by Nilson, who separated it, with ytterbia, from erbia extracted from euxenite and gadolinite. Nilson made an incomplete chemical examination of some of its compounds, but owing to the inadequate amount of material at his disposal he did not at first entirely separate it from ytterbia. Later in the same year Cleve extracted scandia from gadolinite, yttrotitanite, and keilhauite, and described the scandium sulphate, double sulphates, nitrate, oxalate, double oxalates, selenate, acetate, formate, oxide, and hydrate, and gave some of the chief reactions of the new body.

Cleve, working on gadolinite, found that it contained only from 0·002 to 0·003 per cent of scandium, while keilhauite yielded only about 0·005 per cent. He gave results from which he deduced an atomic weight of about 45. Cleve noticed that scandium almost exactly corresponded to the description given by Mendeleeff of his hypothetical element "ekaboron," of atomic weight 44. More recently, in 1880, Nilson, working on somewhat larger quantities of scandia, described and analysed the nitrate, sulphate, selenate, oxalate, and the potassium double sulphate. He found the atomic weight to be 44·03, the mean of four separate and closely concordant determinations. Taking Nilson's data, and re-calculating from them the atomic weight of scandium, using the most recent figures for oxygen and sulphur, I find his atomic weight to be almost exactly 44·1—a figure I have used in the following paper.

In the course of my twenty years' work on the fractionation of the rare earths I have repeatedly tested my products by examining their photographed spectra, using the dominant lines of the various elements as tests for their presence. Scandium has an extremely characteristic group of lines in its spectrum, situated between wave-length 3535·864 and wave length 3651·983, the strongest being at 3613·984, midway between two strong iron lines. By using a part of the spectrum in which this line occupies the centre of the photograph, it is easy to recognise scandium. Detecting the dominant line, the presence of scandium can be verified by reference to the other lines of the group. (See Plate).

Scandium I found in some of my fractions, but only in small quantities. A few years ago I commenced an examination of all the obtainable rare-earth minerals, in order to see if any of them showed more than a trace of scandium. The minerals examined are given in next col.

Of these minerals scandium was detected in auerlite, cerite, cryptolite, keilhauite, koppite, mosandrite, orangite, orthite, pyrochlore, thorianite, thorite, urdite, and wiikite. But while the other minerals contained less than 0·01 per cent of scandium, wiikite was found to contain more than one hundred times that amount.

Wiikite is a black amorphous mineral found with monazite in a felspar quarry at Impilaks, Lake Ladoga, Finland. It is named after Professor Wiik, of Helsingfors (*Min. Mag.*, vol. xiii., p. 379).

I have compared wiikite with a large number of typical rare-earth minerals, and in appearance I find it most resembles yttrotantalite. A thin section under the microscope looks like solidified mud. It is quite amorphous, breaks with a conchoidal fracture, shows no crystalline structure, and has no action on polarised light.

Wiikite is somewhat radio-active. A fragment was laid on a sheet of sensitive film—opaque black paper intervening—for ninety-five hours. Subsequent development revealed a good impression, about equal in strength to what would be given by pitchblende in twenty-four hours. The image was not uniform, and at one point radiation had spread from the mineral over the adjacent part of the sensitive film.

* A Paper read before the Royal Society, April 30, 1908.

Æschynite	Polycrase
Allanite	Pyrochlore
Alvite	Rhabdophane
Auerlite	Samarskite
Baddelite (Ceylon)	Scheelite (Bohemia)
Bastnasite	Scheelite (New Zealand)
Bröggerite	Schorlomite
Cerite	Sipylite
Clevite	Tantalite
Columbite	Thalenite
Cryptolite	Thorianite
Eudialite	Thorite
Euxenite	Thorogummite
Fergusonite (Ceylon)	Tscheffkinite
Fergusonite (Ytterby)	Tysonite
Fluocerite	Urdite
Gadolinite	Wiikite
Hielmite	Xenotime
Homolite	Yttergarnet
Keilhauite	Yttrialite
Knopite	Yttrocerite
Koppite	Yttrogummite
Lanthanite	Yttrotantalite
Monazite	Yttrotitanite
Mosandrite	Zirkelite (Ceylon, sp. gr. 5·0)
Orangite	Zirkelite (Ceylon, sp. gr. 4·42)
Orthite	

The specific gravity of wiikite is 4·85. Its hardness is 6. It is infusible before the blowpipe. It is imperfectly attacked by strong mineral acids and breaks up easily when fused with potassium bisulphate. Heated to full redness in a silica tube it gives off helium, water, and a distinct amount of sulphuretted hydrogen, followed by a white sublimate. The mineral begins to crack at a temperature a little below redness, and, at the approach of redness, gas is evolved with almost explosive violence, the mineral breaking and flying about the tube. A fragment so treated examined under the microscope shows a surface covered with glistening points. With a high power these points are resolved into a mass of minute cubes, curiously regular in form and appearance. Heating drives off 5·83 per cent of its weight; 5·82 of the loss is water and acid vapour, the difference, 0·01 per cent, consists chiefly of helium, with a little hydrogen, carbon dioxide, and a mere trace of neon. The average amount of gas collected from 100 grs. of the mineral was 15·6 cc. Sir James Dewar kindly passed the gases for me over hot oxide of copper and then through charcoal immersed in liquid air. This should absorb and retain everything but helium and the trace of neon. The gas thus purified, after exhaustion to the most luminous point, was sealed in a double-bulb silica tube. The spectrum, visual and photographed, was that of pure helium with a scarcely perceptible trace of neon.

Containing so many bodies, the exact separation of which one from the other is not known, it is at present impossible to give an accurate and complete analysis of wiikite. Moreover, I find the composition varies somewhat in different samples of the mineral. The following is considered a fair approximation of the composition of a typical specimen :—

Tantalic acid with some niobic acid	15·91
Titanic acid and zirconia	23·36
Earths of the cerium group	2·55
Earths of the yttrium group	7·64
Scandia	1·17
Thoria	5·51
Ferrous oxide	15·52
Uranic oxide	3·56
Silica	16·98
Water and gases	5·83
Calcium, manganese, tin, sulphur, &c., unestimated	1·97
	100·00

The percentage of scandia is too low. Owing to the difficulty of separating it completely from the accompanying earths and metallic acids, the amount given is only that which has been obtained in an approximately pure state.

I find the following the best process to extract scandia from wiikite :—The ground mineral is passed through an 80-mesh sieve, then mixed with five times its weight of powdered potassium bisulphate and fused in a clay crucible. At first much frothing occurs, due to the escape of permanent gases and aqueous vapour; this ebullition can be abated by stirring with an iron rod. When in quiet fusion, the heat is raised to full redness for ten minutes and the liquid mass poured on an iron plate. When cold, the melt is finely ground, mixed with water in the proportion of 1 kilo. to 5 litres, and mechanically agitated for about twelve hours. It is then thrown on a linen filter and well washed. This treatment extracts most of the rare earths, together with a little titanic, niobic, and tantalic acids and zirconia, but the bulk of these bodies is left behind.

The solution is supersaturated with ammonia and well boiled; this treatment precipitates all the earths, together with iron, titanic acid, zirconia, &c. The precipitate of crude earths is filtered and well washed.

The precipitated crude earths are converted into oxalates by heating the pasty precipitate in a dish with crystals of oxalic acid added gradually, excess being avoided as much as possible. When cold, the oxalates are filtered off, and the iron, &c., in the filtrate is precipitated with ammonia. As scandium oxalate is slightly soluble in water, the iron precipitate will contain a certain proportion, which must be kept for subsequent working up.

The washed oxalates are dried and ignited; the resulting earths form about 17 per cent of the mineral and contain about 7 per cent of scandia.

The crude oxides are converted into sulphates by heating with sulphuric acid, the excess of acid being driven off by heat—not using too high a temperature. The dry sulphates are agitated with plenty of water, and filtered from a little insoluble residue of metallic acids. Ammonia in excess is then added to the filtrate, and the precipitated oxides are washed, once more converted into oxalates in the manner already described, and the oxalates again washed, dried, and ignited. The ignited oxides are boiled in dilute nitric acid, filtered from a little insoluble matter, and evaporated to dryness. These somewhat complicated operations are to insure the removal of sulphuric and metallic acids, the presence of which interferes with subsequent fractionation.

The earthy nitrates rich in scandium are mixed with an equal bulk of potassium nitrate and fused in large porcelain crucibles with constant stirring until the mass has the appearance of cream—fluid when hot, solidifying on cooling to a white enamel-like mass. On boiling this mass in water, a dense white basic nitrate separates and undecomposed nitrates are left in solution. Scandium and ytterbium, forming easily decomposed nitrates, concentrate in the insoluble end—the "heads"—while the yttrium and cerium earths, whose nitrates are less easily decomposed by heat, are left in the soluble end—the "tails." Fractionation on these lines must now be continued until spectrum photographs show the scandium to be pure. It is not difficult to obtain scandia free from all earths present except ytterbia and yttria; but the final elimination of pure scandia from these earths is a matter demanding much time and patience.

This easy decomposition of the nitrate by heat makes it possible by a systematic series of fractionations to separate scandium from most of the other associated elements. The worst impurity is ytterbium, the nitrate of which is almost as easily decomposed. Fortunately a strong dominant line of the ytterbium spectrum, wave-length 3694·344, occurs at a vacant part of the scandium spectrum, and near the characteristic group of scandium. A sample of scandia is not considered satisfactory if the least trace of this line is seen on an over-exposed spectrum of scandium, and if the atomic weight is higher than 44·1. The atomic

weight of ytterbium being 173, a very little of it as an impurity raises the atomic weight of scandium.

SCANDIUM HYDROXIDE,

$Sc_2O_3,3H_2O = Sc(OH)_3$.

On adding caustic alkali to a solution of a scandium salt the hydroxide comes down as a bulky gelatinous precipitate. It is insoluble in excess of precipitant. In appearance it resembles yttrium hydroxide. It dries in the air at ordinary temperatures to a hard porcelain-like mass and has the composition given above.

Analysis.

5·289 grs. lost on ignition 1·533 grs. of water.

	Theory.		Experiment.
Sc_2O_3	136·200	71·59	71·02
$3H_2O$	54·048	28·41	28·98
	190·248	100·00	100·00

The hydroxide is a very weak base, with a marked tendency to form basic salts. It dissolves readily in dilute acids, forming salts which have a sweet astringent taste. The salts show no absorption spectra.

After ignition, anhydrous scandia, Sc_2O_3, is difficultly soluble in dilute acids in the cold, rather more easily soluble when warmed, and readily soluble in hot strong mineral acids. Strong sulphuric acid poured on ignited scandia attacks it with considerable evolution of heat.

SCANDIUM CARBONATE,

$Sc_2(CO_3)_3,12H_2O$,

comes down as a bulky white precipitate on adding ammonium or sodium carbonate to a soluble salt of scandium. It is almost insoluble in a cold dilute solution of ammonium carbonate, but is moderately soluble in a hot and strong solution of this salt, and as in the same circumstances yttrium carbonate is much less soluble, this difference may be utilised as a basis for a method of separating scandium and yttrium by fractionation.

Scandium carbonate holds carbonic acid very weakly, and concordant analyses are not easy to get. Drying at 100° drives off water and some of the carbon dioxide, leaving a basic carbonate. When freshly precipitated and dried in a current of air at the ordinary temperature, the following formula best agrees with the figures obtained :—

$Sc_2(CO_3)_3,12H_2O$.

At a temperature of 100° this salt loses carbon dioxide and water, and becomes a basic salt of uncertain composition.

Strong ignition drives off all water and carbon dioxide, leaving Sc_2O_3.

HYDRATED SCANDIUM CHLORIDE,

$Sc_2Cl_6,12H_2O$.

The hydrated salt is prepared by dissolving the earth in hydrochloric acid and evaporating on a water-bath. It crystallises from a strong solution as a felt-like mass of fine white needles. The crystals should be pressed many times between filter-paper frequently renewed, and put to dry for a few hours in a desiccator over sulphuric acid. They are somewhat deliquescent, but not so much so as the nitrate, and are readily soluble in alcohol. They have the following composition :—

$Sc_2Cl_6,12H_2O = Sc_2O_3,6HCl,9H_2O$.

Analysis.

1. 6·087 grs. of the pressed chloride left on ignition 1·620 grs. of scandia.
2. 5·960 grs. of the pressed chloride lost 1·836 grs. after remaining in the water-oven at 100° for six hours.

	Theory.		Experiment.
			1 and 2.
Sc_2O_3	136·200	26·34	26·61
6HCl	218·748	42·30	42·58
$9H_2O$	162·144	31·36	30·81
	517·092	100·00	100·00

When heated for six hours to a temperature of 100°, the 9 molecules of water go off, leaving a clear, colourless, and oily liquid, which on cooling solidifies to a white crystalline mass of the composition

$Sc_2Cl_6,3H_2O = Sc_2O_3,6HCl$.

When this salt is gradually heated to redness it gives off 6 molecules of hydrochloric acid with much intumescence, leaving a bulky residue of scandia.

Analysis.

1. 4·235 grs. on ignition left 1·620 grs. of scandia, = 1·049 grs. of scandium.
2. 4·124 grs. were dissolved in water and the scandia precipitated by ammonia. The scandia obtained weighed 1·592 grs., = 1·031 grs. of scandium.

	Theory.		Experiment.	
			1.	2.
2Sc	88·200	24·85	24·77	25·00
6Cl .. .. }	266·748	75·15	75·23	75·00
$3H_2O$ . . }				
	354·948	100·00	100·00	100·00

HYDRATED SCANDIUM BROMIDE,

$Sc_2Br_6,12H_2O$.

Scandium hydroxide or carbonate dissolves easily in hydrobromic acid, and the acid solution evaporated on the water-bath deposits small rhombic crystals, coloured slightly brown by free bromine and very deliquescent. These crystals were collected on filter-paper and dried by pressure between folds of paper frequently renewed. They were then put into a silica weighing bottle, and dried in a desiccator over sulphuric acid.

Analysis.

1. 29·753 grs. of the hydrated bromide gave on ignition 5·068 grs. of scandia.
2. 29·753 grs. of the hydrated bromide lost at 120° 6·207 grs. of water.

	Theory.		Experiment.
			1 and 2.
Sc_2O_3	136·200	17·37	17·03
6HBr	485·808	61·95	62·11
$9H_2O$	162·144	20·62	20·86
	784·152	100·00	100·00

When the hydrated bromide is heated in an air-bath to 120° it loses 9 molecules of water and becomes—

$Sc_2Br_6,3H_2O = Sc_2O_3,6HBr$.

Analysis.

23·546 grs. of the dried bromide left on ignition 5·068 grs. of scandia.

	Theory.		Experiment.
Sc_2O_3	136·200	21·89	21·53
6HBr	485·808	78·11	78·47
	622·008	100·00	100·00

SCANDIUM FLUORIDE,

Sc_2F_6.

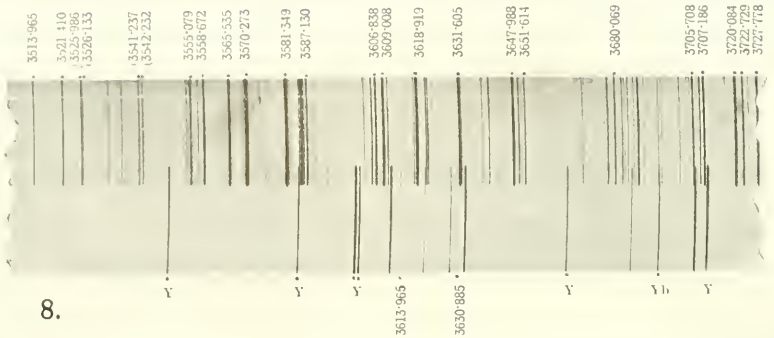
Ignited scandia is attacked by aqueous hydrofluoric acid, forming a semi-transparent gum-like mass, which on boiling

THE SCANDIUM SPECTRUM.

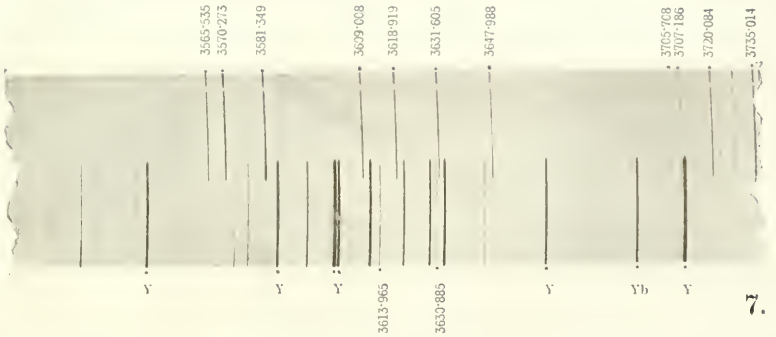
SELECTED GROUPS OF CHARACTERISTIC LINES.

To economise space and avoid unnecessary complications, I give photographs of only those parts of the spectrum containing the most prominent scandium groups. The upper half of each strip shows the iron lines used as standards, with their wave-lengths according to ROWLAND'S measurements. The lower halves contain the scandium lines, with their wave-lengths calculated from the iron standards.

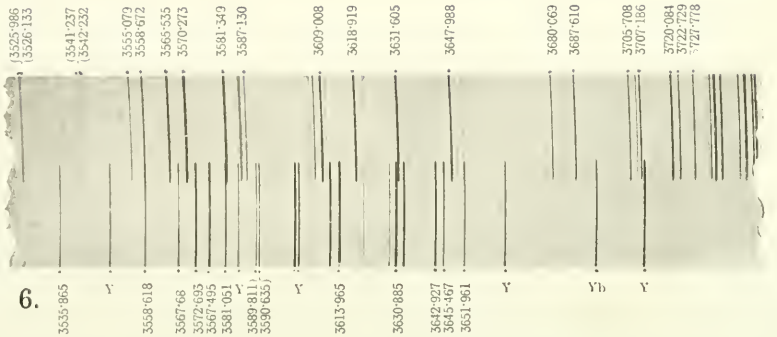
There are also many strong lines in the ultra-violet spectrum of scandium between λ 3535·865 and λ 2300. I have not completed the measurements of these lines, and their description must form the subject of a subsequent communication.



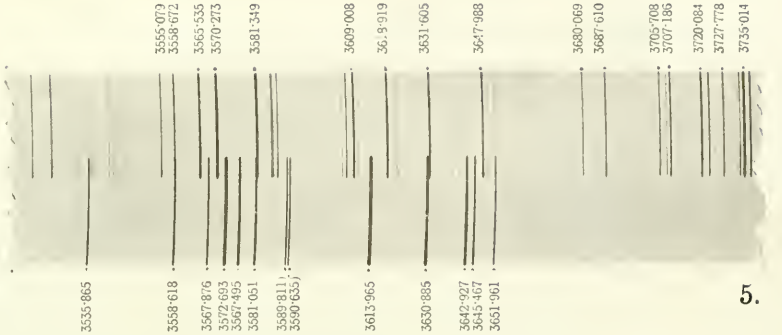
8. Spectrum of crude rare earths from keilhauite, also photographed in the same position as in Spectrum 5. It was from the rare earths from keilhauite that CLEVE prepared scandium.



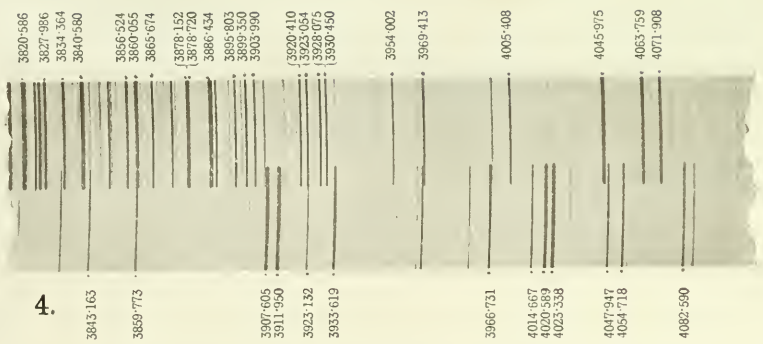
7. Spectrum of crude rare earths from euxenite, also photographed in the same position as in Spectrum 5. It was from euxenite that NILSON first extracted scandium.



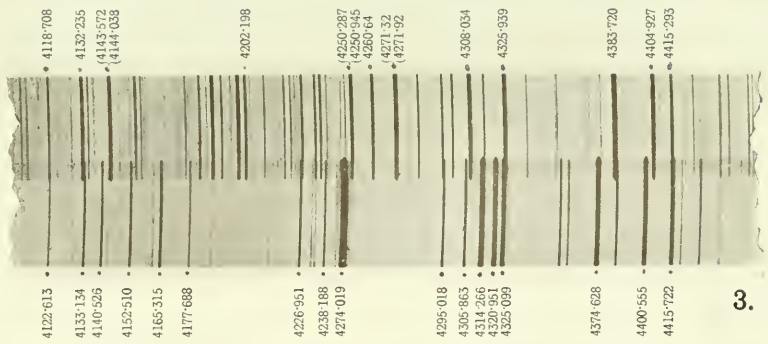
6. Spectrum of crude rare earths from wiikite, photographed in the same position as in Spectrum 5. In addition to the dominant and other lines of scandium, which are marked in wave-lengths, there are seen lines of yttrium and one strong line of ytterbium.



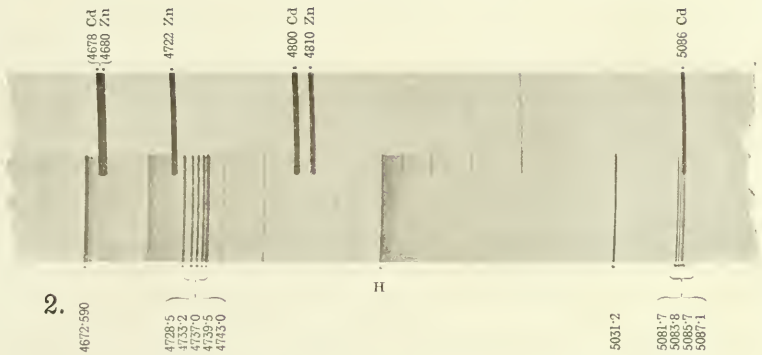
5. Group of lines between λ 3651·961 and λ 3535·865. This is the part of the spectrum which I photograph when minerals are being examined for scandium. The "dominant line," λ 3613·965 occurs here between the iron lines λ 3618·919 and λ 3609·008.



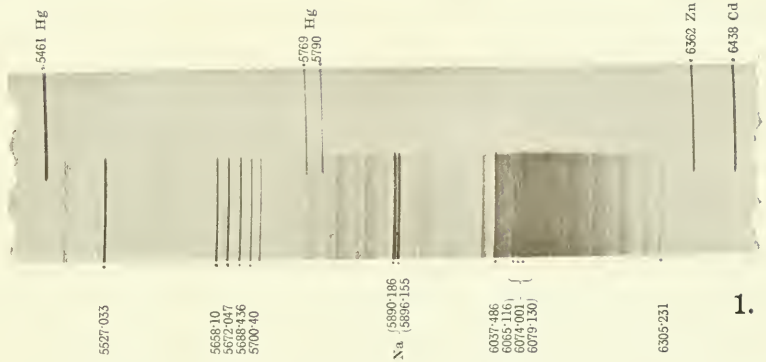
4. Group of lines between λ 4082·590 and λ 3843·163.



3. Group of lines between λ 4415·722 and λ 4122·613.



2. Group of lines between λ 5087·1 and λ 4672·590.



1. Group of visible lines between λ 6305·231 and λ 5527·033.

In the part of the spectrum shown on strips 1 and 2 there are no iron lines suitable for standards. Here, therefore, I have used some good lines of zinc, cadmium, and mercury. Attention is drawn to the comparative intensities of the yttrium lines and the dominant line of scandium in the spectra from the wiikite, euxenite, and keilhauite earths. The spectrum of the earths from gadolinite is not given, as the dominant line of scandium in it is too faint to be reproduced.

changes to a fine white precipitate. This is difficult to filter, and it has great tendency to run through.

When hydrofluoric acid is added to a solution of scandium nitrate or sulphate, a white precipitate comes down. On boiling it becomes milky, resembling the above-described precipitate.

The fluoride dried over sulphuric acid is anhydrous. It slightly loses weight at a red heat, and at a yellow heat it frits together, fusing with difficulty before the blowpipe.

Strong sulphuric acid imperfectly decomposes scandium fluoride. It is completely decomposed by fusion with potassium bisulphate; the melt dissolves in acidulated water, and the solution mixed with ammonia deposits scandium hydroxide.

Analysis.

8·955 grs. of scandium fluoride, decomposed by fusion with potassium bisulphate and precipitated by ammonia, gave 0·0365 grs. of scandia, = 3·9091 grs. of scandium.

	Theory.		Experiment.
Sc_2	88·2	43·62	43·65
F_6	114·0	56·38	56·35
	202 2	100·00	100·00

Scandium Chlorate.

Aqueous chloric acid saturated with scandium hydroxide forms at first a clear colourless liquid; evaporation on the water-bath decomposes it, with evolution of chlorine. On further evaporation, crystals like long needles form on cooling, and the mother-liquor becomes a gummy amorphous mass in which, after standing, appear long needle-shaped crystals. These crystals probably are the perchlorate.

Scandium Perchlorate.

Aqueous perchloric acid easily dissolves scandium hydroxide or carbonate, and the solution evaporated over the water-bath separates into a felt-like mass of rhombic needle-shaped crystals.

Scandium Bromate.

Bromic acid readily dissolves scandium hydroxide, but on evaporating the solution it decomposes, leaving an amorphous gummy mass without crystalline appearance.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 19th, 1908.

Sir William Ramsay, K.C.B., F.R.S., President, in the Chair.

The President announced that the Society had become indebted to Prof. J. Emerson Reynolds, F.R.S., for presenting a bust of Michael Faraday.

Certificates were read for the first time in favour of Messrs. Arthur Clayton, B.Sc., 35, Sisters Avenue, Clapham Common, S.W.; John Charles Jesser Coope, Bulawayo, Rhodesia, S. Africa; Arthur Gordon Francis, B.Sc., 50, Whitbread Road, Brockley, S.E.; Ross Aiken Gortner, M.A., B.Sc., Lincoln, Nebraska, U.S.A.; Frank Higson, Ivy Bank, Castle Street, Haulgh, Bolton; James Henry Hoseason, Alderside, Timperley, Cheshire; Ralph Hough, 14, Longford Place, Victoria Park, Manchester; Percy May, 126, Cazenove Road, Stamford Hill, N.; Frank George Pope, 28, Alcester Crescent, Upper Clapton, N.E.; Philip John Sageman, 160, Brecknock Road, N.

Certificates have been authorised by the Council for presentation to ballot under By-law I. (3), in favour of Messrs. Thomas Boles Allen, M.A., Medical Faculty, McGill University, Montreal; Maung Ba, B.A., Rangoon College, Rangoon; Prince Mom Chow Bhunsri, Saranrome Palace, Bangkok, Siam; Maung San U, Government Laboratory, Rangoon; Herbert M. Shilstone, B.Sc., 410, South Front Street, New Orleans, U.S.A.; Rev. John Watt, M.A., Scottish Churches College, Calcutta.

Of the following papers, those marked * were read:—

*238. "*Meteloidine; a New Solanaceous Alkaloid.*" By Frank Lee Pyman and William Colebrook Reynolds.

Datura meteloides yields 0·4 per cent of total alkaloid, from which 0·13 per cent of hyoscine, 0·03 per cent of atropine, and 0·07 per cent of a new alkaloid, *meteloidine*, have been obtained.

Meteloidine, $C_{13}H_{21}O_4N$, crystallises in tabular needles, melting at 141—142°. It forms crystalline salts, of which the *hydrobromide*, $C_{13}H_{21}O_4N,HBr,2H_2O$ (needles, m. p. 250°), *aurichloride*, $C_{13}H_{21}O_4N,HAuCl_4,\frac{1}{2}H_2O$ (hexagonal plates, m. p. 149—150°), and *picrate* (hexagonal plates, m. p. 177—180°) have been prepared. It is optically inactive, and has no marked physiological action.

It is readily hydrolysed by hot aqueous barium hydroxide, with the formation of tiglic acid and a new base, *teloidine*, according to the equation $C_{13}H_{21}O_4N + H_2O = C_5H_8O_2 + C_8H_{15}O_3N$.

Teloidine crystallises from moist acetone in needles, which contain one molecule of water of crystallisation, and, after drying at 120°, melts at 168—169°. It forms crystalline salts, of which the *hydrochloride*, $C_8H_{15}O_3N,HCl$ (prisms, m. p. above 300°), *hydrobromide*, $C_8H_{15}O_3N,HBr$ (hexagonal plates, m. p. 295°), and *aurichloride*, $C_8H_{15}O_3N,HAuCl_4,\frac{1}{2}H_2O$ (hexagonal plates, m. p. 225) have been characterised.

Attention was drawn to the similarity of the properties of teloidine with those of tropine and oscine.

*239. "*The Affinity of certain Alkaloids for Hydrochloric Acid.*" By Victor Herbert Veley.

Determinations have been made of the affinity values of the nitrogen atoms or amino-groups of certain alkaloids, which, although containing more than one atomic proportion of nitrogen, yet form stable combinations with one molecular proportion of hydrogen chloride, the dihydrochlorides being produced only under special conditions, or not, as yet, having been obtained. It was shown by the application of the methyl-orange method that in all cases the affinity values of these amino-groups are of a widely different order.

In the case of the cinchona alkaloids, the affinity value of one amino-group is rather less than that of a hydropyridine, whilst that of the other is rather lower than that of quinoline. These results are in accordance with the accepted constitution of these alkaloids and the thermoneutrality values obtained by the addition of one and two molecular proportions of hydrogen chloride respectively.

In the case of pilocarpine, the value of one grouping is intermediate between that of ammonia and the limit value of the methyl-orange method, whilst that of the other is equal to those of true amphoteric electrolytes.

A methylglyoxaline was examined on account of the relationship of pilocarpine to these compounds; the value of the two amino-groups and its general behaviour correspond with a diamino-base of the type of hydrazine.

Of the *Nux Vomica* alkaloids, strychnine and brucine were examined; in both cases, the affinity value of one amino-group was beyond the limit value of the methyl-orange method, whilst that of the other corresponded with the betaines, which is in accordance with the views held regarding their constitution.

Discussion.

Dr. Veley, in reply to Dr. Jowett, stated that so far as results had been obtained it appeared probable that if an alkaloid was constituted of two residues, either or both

containing an amino-group, the affinity value of the one was affected by that of the other.

This had been observed more especially in the case of tropine, the parent base of the atropine and cocaine alkaloids, the results for which it was hoped shortly to communicate to the Society.

*240. "*The Relation between Absorption Spectra and Chemical Constitution.* Part XII. *Some Amino-aldehydes and -ketones of the Aromatic Series.*" By Edward Charles Cyril Baly and Effie Gwendoline Marsden.

The absorption spectra of *o*- and *p*-aminobenzaldehyde and the three isomeric aminoacetophenones have been observed; they all exhibit a single broad absorption band which is within the visible region of the spectrum, so that the substances are visibly coloured. The addition of a small quantity of alcoholic hydrochloric acid to the solution of each of the compounds causes a considerable deepening of the colour, which is due to the formation of a new absorption band nearer to the red than the principal band referred to above. This phenomenon does not occur in aqueous solution, and is most evident with the para-isomeride and least with the meta. It has also been observed in the case of tetramethyldiaminobenzophenone and the aminobenzaldoximes. The phenomenon is apparently due to an increased activity of the amino-group, and hence affords an explanation of the catalytic action of mineral acid on the acetylation of amino-compounds.

Discussion.

Dr. Hewitt inquired if the absorption spectrum of *p*-aminobenzaldehyde in presence of a small quantity of hydrochloric acid was measured in absolute alcoholic solution, and he also wished to know how the substance was isolated in a pure condition.

Mr. Baly, in reply to Dr. Lowry, said that the original compound was restored when the acid was neutralised. In reply to Dr. Forster, the absorption spectrum of the hydrochloride was entirely different from that of the base in presence of a trace of alcoholic hydrogen chloride. Considerable difficulty had been experienced in the preparation of *p*-aminobenzaldehyde. It was obtained from *p*-aminobenzaldoxime and then regenerated from its hydrochloride. The melting-point was correct, and, moreover, the condensation product was very different from the aminobenzaldehyde itself in that it was only very slightly soluble in alcohol.

*241. "*Organic Derivatives of Silicon.* Part VIII. *The Resolution of* dl-*Sulphobenzylethylisobutylsilicyl Oxide and the Properties of the Optically Active Acids.*" By Bernard Dunstan Wilkinson Luff and Frederic Stanley Kipping.

dl-*Sutphobenzylethylisobutylsilicyl oxide*,—

$$[SO_3H\cdot C_6H_4\cdot CH_2\cdot SiEt(C_4H_9)]_2O,$$

is resolved into its optically active components by the fractional crystallisation of its salt with *d*-methylhydrindamine; the pure *dAdB*-salt obtained melts at 207—209°, and has $[\alpha]_D + 16{\cdot}7°$ in methyl-alcoholic solution. The specific rotation of the sodium salt of the *d*-acid is $[\alpha]_D + 10{\cdot}4°$. The pure *lAlB*-salt (melting at 207—209° and having $[\alpha]_D$ 17·0° in methyl-alcoholic solution) is obtained by fractionally crystallising the salt of the *dl*-acid with *l*-methylhydrindamine; the specific rotation of the sodium salt of the pure *l*-acid is $[\alpha]_D - 10{\cdot}5°$.

d-*Methylhydrindamine* l-*sulphobenzylethylisobutylsilicyl oxide* and the corresponding *dAlB*-salt, prepared by combining the optically pure acids with *d*- and *l*-methylhydrindamine respectively, are oils at the ordinary temperature.

l-*Menthylamine* d-*sulphobenzylethylisobutylsilicyl oxide* crystallises well (with $4H_2O$), melts when anhydrous at 254—258°, and its specific rotation in methyl-alcoholic solution is $[\alpha]_D - 13{\cdot}9°$. The salt of the *l*-acid is very similar in properties, but melts at 253—257°, and has $[\alpha]_D$ 17·2° in methyl-alcoholic solution. The salt of the *dl*-acid melts at 240—245°, and has $[\alpha]_D - 14{\cdot}7°$.

d-*Bornylamine* d-*sulphobenzylethylisobutylsilicyl oxide* melts at 209—211°; the salt of the *l*-acid melts at 210—212°.

d-*Cinchonidine* d-*sulphobenzylethylisobutylsilicyl oxide* crystallises in needles melting at 171—173°, whereas the salt of the *l*-acid melts at 181—183°; the specific rotations of the two salts, however, are practically identical, having the values $[\alpha]_D - 68{\cdot}5$ and $[\alpha]_D - 69{\cdot}3°$ respectively in methyl-alcoholic solution. The *cinchonidine hydrogen* salts of the *d*- and *l*-acids are crystalline, and decompose at 232—234° and 229—231° respectively.

*242. "*The Action of Phosphorus Pentachloride on the Methylene Ethers of Catechol Derivatives.* Part III. *The Cyclic Carbonates of Dichloro-ethyl- and -propyl-catechol.*" By George Barger.

From α-3 : 4-*methylenedioxyphenyl-αβ-dichloroethane*,—

$$CH_2{<}^{O}_{O}{>}C_6H_3\cdot CHCl\cdot CH_2Cl,$$

b. p. 159—160°/12 mm., or from the corresponding *chlorohydrin*,—

$$CH_2{<}^{O}_{O}{>}C_6H_3\cdot CH(OH)\cdot CH_2Cl,$$

m. p. 95°, b. p. 169—170°/7 mm., the very unstable crystalline *substance*,—

$$CCl_2{<}^{O}_{O}{>}C_6H_3\cdot CHCl\cdot CH_2Cl,$$

m. p. 56°, b. p. 170—174°/6 mm., was obtained; the latter is transformed by formic acid into the cyclic *carbonate*,—

$$O{:}C{<}^{O}_{O}{>}C_6H_3\cdot CHCl\cdot CH_2Cl,$$

b. p. 180—182°/8 mm. Similarly, from *iso*safrole dichloride, the *substances*,—

$$CCl_2{<}^{O}_{O}{>}C_6H_3\cdot CHCl\cdot CHCl\cdot CH_3,$$

b. p. 174·5—175·5°/8 mm., and—

$$O{:}C{<}^{O}_{O}{>}C_6H_3\cdot CHCl\cdot CHCl\cdot CH_3,$$

b. p. 186—189°/8 mm., were obtained. The cyclic carbonates are readily hydrolysed to catechol derivatives, but the latter are so unstable that they have not as yet been obtainable in the pure state.

*243. "*The Synthesis of Thionaphthen Derivatives from Styrenes and Thionyl Chloride.*" By George Barger and Arthur James Ewins.

When styrene halides or allied derivatives are heated with a large excess of thionyl chloride to 180—270°, sulphur compounds result, which are most probably derivatives of thionaphthen. More or less extensive chlorination always takes place; thus $\alpha\beta$-dibromostyrene, $C_6H_5\cdot CHBr\cdot CH_2Br$, yields *hexachlorothionaphthen*, C_8Cl_6S, m. p. 158°. A number of similar derivatives from other styrenes were described.

244. "*The Affinity Constants of Bases as determined by the Aid of Methyl-orange.*" By Victor Herbert Veley.

It was shown that the methyl-orange method, as described in a previous communication (*Trans.*, 1908, xciii., 652 *et seq.*), gives results which are concordant with those obtained by the catalysis of methyl-acetate, inversion of sucrose, and electric conductivity methods. If the last named give accurate results, then the same applies equally to the first, which possesses the advantages of simplicity of apparatus, brevity, and smaller amount of material required.

Determinations have been made of the hydrolysis and affinity constant values of about 50 cyclic bases derived from benzene, pyridine, naphthalene, and quinoline; the mutual relationship and effects produced by the substitution of one or more atomic proportions of hydrogen, whether in the nucleus or side-chain, by various elements or groupings were discussed.

The variation of the several constants, namely, $C_{(H)}$, K_W, and K_b, with temperature was dealt with, and it was shown that in cases which determinations of these constants have been made by the same or different trustworthy methods, the experimental results obtained are in accordance with those calculated by the formula $K_{T1}/K_T = (T_1/T)^m$ (T = absolute temperature). Thus ionic dissociation, whether of water or electrolytes, cannot be differentiated in respect of temperature from any other change, generally regarded, as of a purely chemical nature. The importance of this formula for the purpose of other calculations was also emphasised.

245. "*Study of the Constitution and Properties of the Rhodanides of Inorganic Radicles.*" By Augustus Edward Dixon and John Taylor.

The mean refraction value of the ·NCS group in organic thiocarbimides being about 28·1, as calculated from the formula—

$$M_D = \frac{(\mu_D - 1)p}{d^{t°}_{4°}},$$

whilst that for the ·SCN group in various organic thiocyanates is about 23·3, the authors, by measuring the molecular refraction of the rhodanides, $P(CNS)_3$ and $PO(CNS)_3$, have endeavoured to ascertain the refraction effect of the rhodanic groups in these substances, with the object of deciding whether the groups have the configuration ·NCS or ·SCN.

The number found for the rhodanic group (assuming the three to be of equal value) being in each case near to 28, the authors conclude that, so far as the results of this purely physical method may be relied on as affording trustworthy evidence with respect to the atomic linking, the two rhodanides mentioned have the thiocarbamidic constitutions $P(\cdot NCS)_3$ and $PO(\cdot NCS)_3$ respectively.

Phosphoryl trithiocarbimide yields definite additive compounds with one and with two molecular proportions of aniline, or with one of diphenylamine, the products being nearly insoluble in cold water. By prolonged contact with cold water, by treatment with hot water, or by dissolution in aqueous alcohol, they are hydrolysed, yielding one-third of the contained sulphur as substituted thiocarbamide, and two-thirds as free or combined thiocyanic acid. Phosphorus trithiocarbimide (1 mol.), like the phosphoryl analogue, is precipitated completely from benzene solution by one molecular proportion of aniline; the solid product, when dissolved in cold alcohol, gives the reactions of a thiocarbamide, and is hydrolysed readily into one molecule of phenylthiocarbamide and two molecules of thiocyanic acid. The authors suggest that very pronounced electro-positive or electro-negative character in the inorganic radicle may have power to influence the configuration of the rhodanic group with which it is associated.

246. "*The Electrical Conductivity of Phosphoric Acid.*" By Harry Edward William Phillips.

Pure phosphoric acid was prepared by treating re-distilled phosphorus trichloride with specially purified water at an equable temperature, and oxidising the resulting phosphorous acid by means of pure nitric acid. The hydrochloric acid and the excess of nitric acid were then expelled by heat.

The phosphoric acid thus prepard was a transparent colourless oily liquid, which showed no tendency to crystallise in the higher strengths, but a specimen of 43 per cent solution yielded numerous small, soft, gelatinous crystals spontaneously on cooling. The pure acid neither reddened litmus nor decomposed carbonates.

For the measurement of conductivity, Kohlrausch's telephone method was employed, and a special Wheatstone bridge was made by the author for the purpose, which gave opportunity of very accurate work.

Curves were drawn showing the actual conductivity per cent of the acid at 0°, also a set of curves showing the comparative conductivity per cent of sulphuric, nitric, hydrochloric, and phosphoric acids and sodium and potassium hydroxides. The results obtained were also worked out to molecular conductivities, and these were compared with the nine values previously obtained by Kohlrausch at 18°, and the more extended work of Jones and Bassett at 0°; they were also compared with the corresponding values for the three common mineral acids. Finally, curves of dissociation values, obtained by means of the formula $\frac{\Lambda}{\Lambda_\infty}$, were drawn.

The results seem to bear out the theory of indicators regarding the ionisation of the hydrogen atom in the molecule of phosphoric acid.

247. "*The Molecular Volumes of the Nitrites of Barium, Strontium, and Calcium.*" By Prafulla Chandra Ray.

The molecular volumes of the nitrites of barium, strontium, and calcium in their monohydrated forms are 77·87, 74·59, and 67·24, whilst those of the anhydrous salts are 70·90, 62·54, and 57·56 respectively. The radicle NO_2 of the anhydrous nitrites of these metals occupies a constant volume, namely, 24·2.

248. "*The Formation of some Carbides.*" By John Norman Pring.

An investigation has been made of the direct union of carbon with the elements aluminium, silicon, and iron in the absence of solid and gaseous impurities. Some preliminary experiments were also carried out with magnesium.

An intimate mixture of the metal with highly-purified carbon, both in a very fine state of division, was heated in a suitable apparatus, enabling definite constant temperatures to be maintained over long intervals, and capable of being evacuated to a pressure below 0·01 mm.

The direct union of pure silicon and carbon in a vacuum commences between 1250° and 1300°, and the presence of iron does not apparently facilitate the reaction, nor does carbon monoxide exert any influence between the limits of atmospheric pressure and 0·03 mm.

Aluminium unites directly with pure carbon in a vacuum at its melting-point (650°), forming aluminium carbide, Al_4C_3, and the velocity of the reaction increases with the temperature, proceeding rapidly above 1400°.

Iron unites directly with carbon at about 700° under a pressure of about 0·05 mm.

Magnesium shows evidence of forming a new carbide below 600°, this compound giving some saturated hydrocarbon on decomposition with water or acids.

249. "*4-Chloroacenaphthene.*" By Holland Crompton and Eva Richardis Cyriax.

When acenaphthene in chloroform solution is treated with chlorine (1 mol.) and the solvent evaporated, an oil remains which does not crystallise on standing and from which no crystalline product could be obtained by means of solvents. On distillation, it yields some unchanged acenaphthene, and then, as main product, a distillate passing over at 305—310° which solidifies in the receiver. This consists of almost pure 4-chloroacenaphthene.

4-*Chloroacenaphthene* crystallises from alcohol in colourless leaflets; it melts at 65°, and boils at 309°; its *picrate* crystallises in yellow needles, melting at 133°. On oxidation by sodium dichromate in acetic acid solution, it yields a chloronaphthalic acid, the anhydride of which melts at 198° and the imide at 278°. When the calcium salt of this acid is heated with soda-lime, naphthalene is obtained, mixed with a little α-chloronaphthalene. If the copper salt is used in place of the calcium salt, α-chloronaphthalene is produced with little naphthalene. On fusing with potassium hydroxide at 250—260°, the acid is converted into 4-hydroxynaphthalic acid, the anhydride of which melts at 257°; this acid had previously been obtained by Graebe from 4-bromonaphthalic acid (*Annalen*, 1903, cccxxvii., 77). The formation of this 4-hydroxynaphthalic acid and of α-chloronaphthalene show that the acid is 4-chloronaphthalic acid, and confirm the constitution given to the chloroacenaphthene.

250. "*Some Molecular Compounds of Styphnic and Picric Acids.*" By Charles Stanley Gibson.

The following compounds have been prepared :—

Acenaphthene styphnate, $C_{12}H_{10},C_6H(OH)_2(NO_2)_3$, crystallising in long orange-coloured prisms melting at 153—154° ; *phenanthrene styphnate*, $C_{14}H_{10},C_6H(OH)_2(NO_2)_3$, crystallising in yellowish red needles melting at 125—126° ; *bromonaphthalene styphnate*, $C_{10}H_7Br,C_6H(OH)_2(NO_2)_3$, crystallising in small, bright yellow needles melting at 107 — 108° ; *m-nitroaniline styphnate*, $NH_2{\cdot}C_6H_4(NO_2),C_6H(OH)_2(NO_2)_3$, crystallising in pale yellow needles melting at 137° ; and *m-nitroaniline picrate*, $NH_2{\cdot}C_6H_4(NO_2),C_6H_2(OH)(NO_2)_3$, crystallising in yellow radiating needles melting at 143°.

NOTICES OF BOOKS.

The Air and Ventilation of Subways. By George A. Soper, Ph.D. New York : John Wiley and Sons. London : Chapman and Hall, Limited. 1908.

In this book the reports which have appeared in the "Transactions of the Rapid Transit Commissioners" are summarised, and edited in such a way as to make them interesting to the general public. Additional matter relating to the characteristics of good and bad air and the general theories of ventilation has been worked up to form a preface for the benefit of those who have had no training in sanitary science ; in the chapter on methods of ventilating, the formulæ for calculating the velocity of air, quantities of air delivered, &c., are collected, but it has not been considered necessary to explain in full the methods of arriving at the formulæ, to follow which would require some considerable knowledge of the principles of mechanics. The systems of ventilation in use in the subways of various large towns are described, and special attention must be called to the diagrams showing the air currents set up by express and other trains ; in the preparation of these much ingenuity has been expended, and the results are most interesting. The bacteriological and chemical methods of analysing the air are illustrated graphically by many charts ; the investigations related to temperature, humidity, odour, bacteria, dust, and carbon dioxide. Oxygen determinations were discontinued after about eighty had been made, for the differences obtained for subway and street air were only trifling. Ozone was not determined, and the author appears to favour the opinion that it does not actually exist in the air. The final chapter deals with the health of subway employés, which has been subjected to a careful and thorough investigation ; though possibly some of the figures tabulated are slightly misleading, on the whole the results obtained are not disquieting ; the presence of the black metallic dust, composed principally of iron, appears to constitute the most serious source of danger to health.

Thirty-second Annual Report of His Majesty's Inspectors of Explosives. London : Wyman and Sons, Ltd. 1908.

The annual report of His Majesty's Inspectors of Explosives for the year 1907 contains the usual tables relating to accidents, authorised explosives, &c. In the report of the chemical advisers details are given of the recently worked out methods of testing various kinds of explosives for mercury. It has been found that specially constructed spectrum tubes are necessary, and different explosives require various modifications of the method, which is very delicate and reliable. A report is also included on some experiments on the dangers of coal-dust, samples of which were subjected to tests under varying conditions, to determine under what circumstances they were dangerous, and whether any relations could be established between the constituents of a coal-dust and its sensitiveness.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvii., No. 17, October 26, 1908.

Mercurous Nitrate as a Micro-chemical Reagent for Arsenic.—G. Denigès.—The author has recently shown that characteristic crystals of arsenic, as arsenic acid, can be obtained on a glass plate by the use of ammoniacal or acetic silver nitrate or by magnesia mixture. By very slightly modifying the method, mercurous nitrate can be used for the same purpose, and similar crystals are obtained provided that the detailed directions given by the author are carefully followed.

Oxydasic Phenomena produced by Colloidal Iron Ferrocyanide.—J. Wolff.—In a feebly alkaline solution colloidal iron ferrocyanide acts like an oxydase towards hydroquinone, and the phenomenon in continuity and the disparity between cause and effect may be compared with the most energetic diastatic actions. It may be explained by supposing that the alkali favours the oxidation of the phenol, and consequently its attack by the iron salt acting like an oxydase. Some salts of manganese oxidise hydroquinone, and it is only necessary to add to them one hundred times less iron (in the form of ferrocyanide) than the amount of manganese present to double the velocity of the reaction.

Action of Bromine on Ether. Monobromaldehyde.—Ch. Mauguin.—A mixture of bromine, water, and ether when exposed to light is decolorised, the action being very rapid in sunlight. When all action is over, two layers of liquid are obtained ; the lower is aqueous and contains large quantities of hydrobromic acid, and the upper contains an aldehyde which gives a white crystalline solid melting at 146° with urethane. This solid is the condensation product of monobromaldehyde with urethane, and with 10 per cent sulphuric acid it yields monobromaldehyde in aqueous solution.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xli., No. 14, 1908.

Preparation of Sulphinic Acids.—Emil Knoevenagel and James Kenner.—Friedel and Craft's reaction can conveniently be used to prepare aromatic sulphinic acids, and yields of on an average 80 per cent can be obtained if the reaction occurs at a low temperature and if it is started by leading in dry hydrochloric acid. The aluminium chloride formed must not be decomposed by acids but by alkalis, the alkaline salts being subsequently decomposed by acids. Phenol ethers react with sulphur dioxide and aluminium chloride without the addition of hydrochloric acid in the cold, the equation being $RO.C_6H_5 + SO_2 = RO.C_6H_4.SO_2H$. The reaction readily goes further to the sulphoxides $2RO.C_6H_5 + SO_2 = H_2O + (RO.C_6H_4)_2SO$, and thence to the sulphonium compounds—

$$3RO.C_6H_5 + SO_2 + AlCl_3 = AlCl_2.OH + (RO.C_6H_4)_3SCl.$$

Hydrochloric acid accelerates the formation of sulphinic acids, especially from aromatic hydrocarbons and sulphur dioxide in presence of aluminium chloride, so possibly the acid chloride of sulphurous acid reacts as follows :— $C_6H_6 + HSO_2Cl = HCl + C_6H_5.SO_2H$, but it is more probable that a compound of sulphur dioxide and aluminium chloride of the composition $Cl.SO_2.AlCl_2$ is formed. $C_6H_6 + Cl.SO_2.AlCl_2 = HCl + C_6H_5.SO_2.AlCl_2$.

Cerium Sulphides.—Wilhelm Biltz.—Cerium sesquisulphide can readily be obtained by sulphating cerium dioxide with sulphuretted hydrogen at a bright red heat, or by heating cerous sulphate in a current of sulphuretted hydrogen. At a lower temperature the disulphide is

formed. The sesquisulphide is a crystalline dark brown powder which is stable in air and in water. It dissolves in dilute acetic acid in the cold, and also in dilute hydrochloric and sulphuric acids. The disulphide does not appear to be a derivative of tetravalent cerium corresponding to the dioxide, but it is rather to be regarded as a polysulphide of formula $Ce_2S_3.S$. Cerium disulphide decomposes at 720°. The sesquisulphide melts between 1400° and 1500°, undergoing decomposition. It is stable in an atmosphere of pure hydrogen at a red heat.

Action of Arsenite and Cyanide on Thiosulphonic Acid Salts.—A. Gutmann.—When an arsenite or cyanide acts on thiosulphate, sulphite and monosulphoxy arsenate or rhodanate are formed :—

$$S_2O_3Na_2 + AsO_3Na_3 = SO_3Na_2 + SAsO_3Na_3,$$
$$S_2O_3Na_2 + NCK = SO_3Na_2 + NCSK.$$

The action of arsenite and cyanide on arylthiosulphonic acid salts is similar, sulphinic acids being formed instead of sulphites :—

$$RS_2O_2Me + AsO_3Na_3 = RSO_2Me + SAsO_3Na_3,$$
$$RS_2O_2Me + NCK = RSO_2Me + NCSK.$$

The liberation of sulphur by thiosulphonic acid salts depends on the formation of a yellow intermediate product, MeOSH, an alkalihydropersulphide. These reactions show the peracid character of thiosulphonic acid salts, the constitution of which must be expressed by the formula

$$R—S(=O)—S—OMe.$$

Reaction between Silver Sulphide and Silver Sulphate. Preparation of Dark coloured Glass.—O. Sackur.—When a mixture of silver sulphide and sulphate is heated above 300°, sulphur dioxide and metallic silver are formed. Attempts to determine the equilibrium pressure of the mixture failed, the only result being the proof that the pressure is greater than ten atmospheres at 300°. If the mixture is heated in a tube of ordinary Thuringian glass the latter acquires a brown colour below 400° ; this colour becomes darker and turns reddish when the mass is left in contact with the glass for some time. It is not distributed uniformly throughout the whole mass, but only over a relatively thin surface layer. Glass coloured by this method absorbs the blue and blue-green rays of the spectrum almost completely, and the yellowish green rather less, and vessels thus coloured may very conveniently be used for photographic purposes to absorb the most actinically active rays. When the brown glass is heated in a Bunsen flame tempering colours are produced owing to the formation of a very thin layer of metallic silver on the surface. A distinct silver white layer is obtained by heating in the blowpipe flame. The brown and reddish-brown glass possesses a small but decided conductivity for the electric current at the ordinary temperature.

Silicon Acids and their Derivatives.—Wilhelm Melzer.—When a molecule of magnesium halogen alkyl acts on silicon tetrachloride, silicon alkyl trichlorides are formed :—$RMgX + SiCl_4 = RSiCl_3 + MgXCl$ (where R denotes an alkyl and X a halogen). These are converted into the corresponding silicon acids of the type R.SiOOH by water, and into orthosilicon acid esters of the type $R.Si(OC_2H_5)_3$ by alcohol. Every trace of moisture must be avoided, especially in experiments with chlorides. By this method the author has prepared various alkyl silicon haloids, *e.g.*, silicon propyltrichloride, $C_3H_7.SiCl_3$, a clear liquid fuming in air and possessing a piercing smell, and also silicon acids, *e.g.*, silicobutyric acid, $C_3H_7.SiOOH$, and their esters.

Lowest Oxides of Sulphuretted Hydrogen.—Emil Fromm.—The lowest oxides of sulphuretted hydrogen are sulphur hydrate, H_2SO, and sulphoxylic acid, H_2SO_2. Sulphur hydrate is not known either free or in inorganic compounds. Derivatives of it are the sulphoxides, R.SO.R, and the hypothetical compounds, R.SOH, the existence of which has, however, never been demonstrated with certainty. All organic disulphides with adjacent double bonds of general formula $\begin{matrix} X:C.S.S.C:Y \\ \dot{R} \quad\quad \dot{R}_1 \end{matrix}$ are decomposed by water, alkalis, and amines, giving elementary sulphur. The author's experiments have proved that sodium tetrathionate also yields elementary sulphur, and thus decomposes in exactly the same way as organic disulphides with adjacent double bonds, thus : $Na_2S_4O_6 + H_2O = S + NaHSO_4 + NaHS_2O_3$. Sodium ethyl thiosulphate and the aromatic disulphides give no elementary sulphur on hydrolysis, but in all probability the hypothetical oxidation product R.SOH is formed. This substance is a strong oxidising agent, and is unstable in alkaline solution, readily giving mercaptan and sulphinic acid, $2R.SOH = R.SH + R.SOOH$. Sulphoxylic acid has not yet been obtained in the free state ; complicated salts of it are the hydrosulphites. A simple salt of sulphoxylic acid, zinc sulphoxylate, $ZnSO_2$, has been prepared by the action of zinc dust on an ethereal solution of SO_2Cl_2, but the compound has not yet been isolated. Aldehydes react with hydrosulphite in presence of alkali according to the equation—

$$R.CHO + Na_2S_2O_4 + NaOH = R.CH(OH).SO_2Na + Na_2SO_3.$$

The acid sulphoxylate may be added to the aldehyde in such a way that oxysulphinic acid is formed, $R.CH(OH).SO_2Na$, or esters of sulphoxylic acid may result, $R.CH(OH).O.SO.Na$ or $\begin{matrix} R.CHOH.O.SNa \\ \ddot{O} \end{matrix}$, or derivatives of orthosulphoxylic acid of formula $\begin{matrix} R.CH.O.S.Na. \\ \dot{O} \diagup\diagdown OH \end{matrix}$ The investigation of the aldehyde and ketone sulphoxylates, especially rongalite (formaldehyde sulphoxylate), shows that in all probability rongalite is an ester of sulphoxylic acid and not an oxymethane sulphinic acid. Its formula may be—

$$HO.CH_2.O.SO.Na \quad \text{or} \quad \begin{matrix} O.... \\ H_2\dot{C}.O.S.Na, \\ \quad\quad \dot{O}H \end{matrix}$$

and possibly it reacts according to both formulæ. In the dibenzyl derivative the Na and the H of the hydroxyl group are both replaced by C_7H_7.

Carbon Suboxide.—Otto Diels and Leonid Lalin.—Although carbon suboxide is unsaturated, it shows only a comparatively slight tendency to form addition products except with formic and acetic acids—addition products with which are readily obtained. They have, however, been prepared in small quantities only, for even at low temperatures the two substances react according to the equation $C(=CO)(=CO) + 2HCO.OH = 2CO + CH_2(COOH)_2$. Liquid sulphur dioxide is a solvent in which the addition of formic acid to carbon suboxide can very conveniently be studied. The addition product is thus found to be a crystalline substance which is quite stable as long as precautions are taken against the presence of moisture and a rise of temperature. The compound contains two molecules of formic acid to one of carbon suboxide, and corresponds to the empirical formula $\left[C(=CO)(=CO) + 2H.COOH\right]$. It seems probable that the characteristic linkage of carbon suboxide is still present in the compound, and that it is a mixed anhydride of malonic and formic acids, although not of normal constitution. Its formula appears to be

$$C\begin{matrix} \diagup C(OH)=CH(COOH) \\ \diagdown C(COOH)=CH(OH) \end{matrix}.$$

On heating, the molecule is decomposed into $2CO$ and $CH_2(COOH)_2$. Acetic acid and carbon suboxide also react in sulphur dioxide, the product being a syrup which, when distilled in a low vacuum, gives acetic acid anhydride and leaves a syrupy residue. The

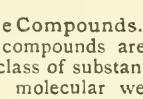
latter probably consists of monomolecular malonic acid anhydride, for with water it yields almost the theoretical quantity of malonic acid.

Formic and Acetic Acid Salts of Chromium.—A. Werner.—The formates and acetates of chromium can be divided into two groups:—(*a*) Normal salts; (*b*) complex salts. The normal salts may be prepared in crystalline form by adding the organic acid to the dihydroxysulphate—

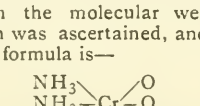
$$\left[Cr\begin{matrix}(OH)_2\\(OH_2)_4\end{matrix}\right]_2SO_4+6HX=2\,[Cr(OH_2)_6]X_3+H_2SO_4.$$

The formate is greenish grey and the acetate blue-violet. The stability decreases as the magnitude of the fatty acid residue increases, the butyrate being so unstable that it decomposes spontaneously after a few days. All fatty acid hexaquochromium salts dissolve in much water with a blue-green coloration, due to hydrolytic dissociation. When moist chromium hydrate is heated with formic acid till it all dissolves, dark green crystals separate out on cooling. These have the formula $Cr_3\begin{matrix}(OH)_2\\(O.COH)_7\end{matrix}+5H_2O$. With nitric acid they give crystals of the composition $[Cr_3(O.COH)_6(OH)_2]NO_3+5H_2O$. Other salts of the same type can be prepared by the action of mineral acids on the nitrate.

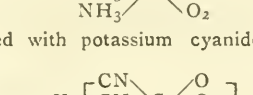
Chromium Tetroxide Compounds.—E. H. Riesenfeld.—Chromium tetroxide compounds are not perchromates but belong to a special class of substances. To determine their composition the molecular weight of chromium tetroxide triammin was ascertained, and it was found that the constitutional formula is—



When treated with potassium cyanide a tricyanide of formula—



is obtained. When an aqueous solution of chromic acid is treated with potassium cyanide and hydrogen peroxide, according to the concentration the tricyanide is formed, or a salt of composition, $K_5\,(CrO_4)_2(CN)_5]+5H_2O$. This last has the constitutional formula—



and is the first known case of a complex salt in which a complex occupies a co-ordination position in a complex salt exactly similar to itself. It seems most probable that the chromium tetroxide compounds are to be regarded as compounds of hexavalent chromium.

Oxalyl Chloride.—H. Staudinger.—A good yield of oxalyl chloride may be obtained by allowing a molecule of anhydrous oxalic acid to act on two molecules of phosphorus pentachloride. A lower yield of the same product is obtained if hydrated oxalic acid is used. Oxalyl chloride is a colourless liquid boiling at 64°. With water it yields carbon dioxide, carbon monoxide, and hydrochloric acid quantitatively, no oxalic acid being formed. With dimethylaniline it gives dimethylaminobenzoylformic acid chloride, or with excess of the base tetramethyldiaminobenzile.

MISCELLANEOUS.

Royal College of Science.—The first Annual Dinner of old students of the Royal College of Science is to be held at the Criterion Restaurant on December 9th. Mr. H. G. Wells (1884-87), who was the first editor of the College Magazine, will preside, and the guests will include Mr. Arthur Acland, Sir Francis Mowatt, Mr. Grant Ogilvie, Dr. Bovey, Dr. Miers, and Professors Tilden and Judd. Tickets may be obtained from Mr. T. Ll. Humberstone, Hon. Secretary of the Dinner Committee, 3, Selwood Place, London, S.W. It is expected that the Dinner will lead to the formation of an Association of Old Students of the College.

Institute of Chemistry.—The following candidates passed the Final Examination for the Associateship in the Branch of Biological Chemistry, held from Oct. 19 to 23:—E. B. Anderson, B.Sc. (Lond. and Birm.); F. G. S. Baker, M.A. (Oxon.): H. L. Gammon; and A. R. Smith, B.Sc. (Manchester). The following Associate also presented himself for the Examination, and was awarded the Certificate: J. H. Totton, B.A., B.Sc. (R.U.I.). The Examiner in Biological Chemistry was Dr. Arthur Harden, F.I.C., and the Examiners in General Chemistry were Mr. Bertram Blount, F.I.C., and Professor Herbert Jackson, F.I.C.

The Royal Society.—At the Annual Meeting, November 30th, 1908, the following Officers and Council were elected:—President: Sir Archibald Geikie, K.C.B., D.C.L., Sc.D., LL.D. Treasurer: Alfred Bray Kempe, M.A., D.C.L. Secretaries: Prof. Joseph Larmor, D.Sc., D.C.L., LL.D., and Prof. John Rose Bradford, M.D., D.Sc. Foreign Secretary: Sir William Crookes, D.Sc. Other Members of the Council: Sir George Howard Darwin, K.C.B.; Prof. James Cossar Ewart, M.D.; Sir David Gill, K.C.B.; John Scott Haldane, M.D.; Charles Thomas Heycock, M.A.; Prof. Horace Lamb, D.Sc.; Prof. Hector Munro Macdonald, M.A.; Frederick Walker Mott, M.D.; The Hon. Charles Algernon Parsons, C.B.; Prof. William Henry Perkin, Ph.D.; Prof Edward Bagnall Poulton, D.Sc.; Lieut.-Col. David Prain, C.I.E.; Sir Arthur William Rücker, D.Sc.; Rt. Hon. Sir James Stirling, M.A.; Prof. Frederick Thomas Trouton, Sc.D.; William Whitaker, B.A.

Physical Society Exhibition.—At the Exhibition to be held on Friday evening, December 11 (from 7 to 10), at the Royal College of Science, South Kensington, the following firms will be exhibiting:—Messrs. Cambridge Scientific Instrument Co.; Casella and Co.; A. C. Cossor, Ltd.; J. H. Dallmeyer, Ltd.; Elliott Bros.; Everett, Edgcumbe, and Co.; Gallenkamp and Co., Ltd.: Gambrell Bros.; J. J. Griffin and Sons, Ltd.; A. Hilger, Ltd.; Indiarubber, Gutta-percha, and Telegraph Works Co.; Marconi's Wireless Telegraph Co.; Nalder Bros. and Thompson; Newton and Co.; R. W. Paul; James Pitkin and Co.; Siemens Bros. and Co.; Snell and Tinsley; J. Swift and Son; Alexander Wright and Co.; and Carl Zeiss, Ltd. From the Programme, of which we have received an advance proof, there appear to be many items of considerable interest to both physicists and electrical engineers. We understand that invitations have been given to the Institution of Electrical Engineers, the Faraday Society, the Optical Society, and the Röntgen Society. Admission, however, except to Fellows of the Physical Society, will be by ticket only, and therefore members of the Societies just mentioned desiring to attend the Exhibition should apply to the Secretary of the Society to which they belong.

MEETINGS FOR THE WEEK.

MONDAY, 7th.—Royal Society of Arts, 8. (Cantor Lecture). "Twenty Years Progress in Explosives," by O. Guttmann.

—— Society of Chemical Industry, 8. "Cellulose and Chemical Industry," by C. F. Cross and E. J. Bevan.

WEDNESDAY, 9th. Royal Society of Arts, 8. "Kinematography in Natural Colours," by G. A. Smith and C. Urban.

THURSDAY, 10th.—Royal Society of Arts, 4.30. "The Birds of India," by Douglas Dewar, I.C.S.

FRIDAY, 11th.—Physical, 7. (At the Royal College of Science, South Kensington). Exhibition of Apparatus.

THE CHEMICAL NEWS.

Vol. XCVIII., No. 2559.

ON SCANDIUM.*

By Sir WILLIAM CROOKES, D.Sc., F.R.S.

(Continued from p. 277).

Scandium Sulphate, $Sc_2(SO_4)_3,6H_2O$.

Scandium hydroxide easily dissolves in dilute sulphuric acid; after ignition the oxide dissolves with difficulty in dilute, but readily in strong acid, with evolution of heat. The excess of sulphuric acid must be driven off carefully, when the anhydrous sulphate is left behind in the form of a fine white powder.

Nilson gives the formula of the anhydrous salt, $Sc_2O_6,3SO_2$. He says: "It loses acid at a high temperature, and leaves pure scandia. The salt treated with water only gives at first a milky liquid, the anhydrous salt combines very slowly with water, and then re-dissolves. On heating, a clear solution is immediately obtained." According to Cleve, "Sulphuric acid gives with scandia a white and bulky mass of sulphate, resembling thorium sulphate when it separates by heat. The sulphate does not form distinct crystals." It is very soluble in water, and a strong solution when heated does not deposit crystals, in that respect differing from most of the other rare-earth sulphates. The solution may be evaporated to a supersaturated syrup, which, standing in the cold for some hours, deposits crystals of the 6-hydrate. One hundred parts of the saturated solution at 12° were found to contain 44·5 parts of anhydrous scandium sulphate. Scandium sulphate is not deliquescent in the ordinary air of a room even in damp weather, and is insoluble in alcohol. On mixing 100 grs. of anhydrous scandium sulphate with the same quantity of water, the temperature rose in a few minutes from 14° to 21°.

On adding absolute alcohol to a stroug solution of scandium sulphate the solution becomes milky, and a heavy oily-looking liquid sinks to the bottom. This may be separated by filtration through paper moistened with alcohol, when the residue is left as a viscous liquid which on exposure to the air becomes thicker. This oily-looking liquid has the composition of the 6-hydrate sulphate.

When strongly heated, the sulphate decomposes, leaving pure scandia. It is, however, difficult to drive off all the sulphuric acid from the sulphate even by heating the crucible containing it before the blowpipe. The best way to decompose scandium sulphate is first to ignite it to the highest temperature of a Bunsen burner, then to moisten with water and add a little ammonium carbonate. Dry and ignite again, and pure scandia is left free from sulphuric acid.

Nilson says: "This salt separates from a syrupy solution in small globular aggregates. It is inalterable in the air, it loses four molecules of water at 100°, and the rest at a higher temperature." He found on analysis 14·26, 14·46, and 7·16, 7·29 of H_2O, instead of 14·88 and 7·44.

I have crystallised this sulphate from a syrupy aqueous solution; it is dried by repeated pressure between many folds of blotting paper.

Analysis.

1. 18·156 grs. of the crystallised 6-hydrate, finely powdered, and heated to 100° for three hours, lost 2·602 grs. of water, leaving a 2-hydrated sulphate.
2. 20·725 grs., kept in a desiccator over sulphuric acid for 170 hours, lost 1·561 grs. of water, leaving a 4-hydrated sulphate.
3. 29·138 grs. left on ignition 8·068 grs. of scandia.
4. 31·508 grs. of the liquid sulphate, precipitated from solution on adding alcohol containing a little ether, were dissolved in water, and the scandia precipitated by ammonia. When dried and ignited it weighed 8 624 grs.

	Theory.		Experiment.
			1, 2, 3, and 4.
Sc_2O_3	136·200	28·11	27·53
$3SO_3$	240·180	49·58	50·61
$2H_2O$	36·032	7·44	7·53
$4H_2O$	72·064	14·87	14·33
	484·476	100·00	100·00

The 6-hydrate effloresces in a dry atmosphere, and loses one molecule of water, becoming the 5-hydrate, which appears to be the most stable hydrate at ordinary temperatures:—

$Sc_2(SO_4)_3,5H_2O$.

Analysis.

1. 16·619 grs. of the 5-hydrate, heated to 150°, lost 3·206 grs. of water.
2. 16·619 grs., after drying as described and igniting to a yellow heat, left 4·878 grs. of scandia.
3. 15·608 grs. of the 5-hydrate, heated *in vacuo* at 100° for twenty hours, and then for ninety minutes at 150°, lost 3·153 grs. of water. Ignited to a full yellow heat, it left 4·558 grs. of scandia.
4. 38·819 grs., heated to just below visible redness, lost 8·019 grs. of water. (At this temperature a trace of basic sulphate is formed. This accounts for the excess over the theoretical loss of water).

	Theory.		Experiment.				Mean.
			1.	2.	3.	4.	
Sc_2O_3 ..	136·20	29·20	—	29·35	29·20	—	29·27
$3SO_3$ ..	240·18	51·49	—	—	—	—	50·68
$5H_2O$ ..	90·08	19·31	19·29	—	20·20	20·66	20·05
	466·46	100·00					100·00

Anhydrous Scandium Sulphate.

$Sc_2(SO_4)_3$.

When the hydrated sulphate is heated to 250° it loses the whole of the water and becomes anhydrous. Its composition now is $Sc_2(SO_4)_3$.

At a bright yellow heat all the sulphuric acid goes off.

Analysis.

1. 30·716 grs. left on ignition 11·092 grs. of scandia.
2. 18·907 grs. left on ignition 6·827 grs. of scandia.

Synthesis.

3. 6·817 grs. of ignited scandia, converted into sulphate, yielded 18·907 grs. of scandium sulphate.

	Theory.		Experiment.		
			1.	2.	3.
Sc_2O_3 . ..	136·20	36·19	36·11	36·11	36·06
$3SO_3$	240·18	63·81	63·89	63·89	63·94
	376·38	100·00	100·00	100·00	100·00

When the anhydrous sulphate is heated to dull redness it loses one molecule of SO_3, and becomes a basic salt of the composition—

$Sc_2O(SO_4)_2$.

Synthesis.

4·622 grs. of ignited scandia were dissolved in strong sulphuric acid, the excess of acid driven off by heat, and the dry sulphate heated to dull redness. It weighed 10·121 grs.

* A Paper read before the Roya Society, April 30, 1908.

	Theory.		Experiment.
Sc_2O_3	136·20	45·97	45·67
$2SO_3$	160·12	54·03	54·33
	296·32	100·00	100·00

Scandium and Potassium Double Sulphate, $3K_2SO_4,Sc_2(SO_4)_3$.

The behaviour of the double sulphates of potassium and the rare-earth metals is usually considered to govern their position in the broad groups into which they are divided. If the double sulphate is insoluble in a saturated solution of potassium sulphate the earth is supposed to belong to the cerium group, while if the double sulphate is soluble the earth is said to be one of the yttrium group. According to Cleve (*Comptes Rendus*, vol. lxxxix., p. 419, August 18, 1879):—"Potassium sulphate in concentrated solution gives rise to the separation of a double salt, a crystalline powder, soluble in a saturated solution of potassium sulphate." Cleve gives the composition of the double salt as $Sc_2O_3,3SO_3+2K_2O,SO_3$. On the other hand, Nilson says (*Comptes Rendus*, vol., cxi., p. 118, July 12, 1880):—"Scandium sulphate in a saturated solution of potassium sulphate gives a double salt, completely insoluble. . . . It dissolves with difficulty in water, even boiling, and not at all in a saturated solution of potassium sulphate. . . . The composition of the double salt, $3K_2O_2SO_2+Sc_2O_63SO_2$, shows that scandium belongs to the group of gadolinite and cerite metals, all these metals giving salts of the same typical composition."

In view of these diametrically opposite statements I have taken especial pains to ascertain the true behaviour of the double salt.

17·717 grs. of re-crystallised scandium sulphate, found by analysis to be pure, were dissolved in water in a flask. The calculated quantity of potassium sulphate to unite with the 17·717 grs., and to make a saturated solution in the water added, was then weighed out, and 5 per cent additional potassium sulphate was added to ensure complete saturation. This was dissolved in boiling water, put into the flask containing the scandium sulphate, and water up to 250 cc. was added. The flask was securely corked, and put into a mechanical agitator, where it was shaken continuously for twenty-five hours. At first, when the two salts were mixed, no precipitation of double salt was visible, but after a short time there appeared a fine granular precipitate, which gradually increased as the shaking proceeded.

At the end of twenty-five hours the precipitated double sulphate was filtered off and washed with 100 cc. of cold saturated solution of potassium sulphate. The filtrate was heated, ammonia added, and the whole well boiled. A very slight precipitate of scandia came down which, when filtered, washed, and ignited, weighed 0·414 gr., equivalent to 1·473 grs. of scandium sulphate in solution, the rest of the sulphate being in the insoluble precipitate. It therefore follows that for every 100 parts of the double sulphate 8·32 per cent are soluble and 91·68 per cent are insoluble in the amount of saturated solution of potassium sulphate employed.

The insoluble double salt was washed with boiling water to remove the little excess of potassium sulphate, until its bulk was reduced about one-half. It was then dried and analysed.

My own analytical results agree closely with Nilson's formula. As Cleve distinctly says that the double sulphate is soluble in a saturated solution of potassium sulphate, it is probable he was not working on the true double salt.

The scandia in the aqueous washings was also determined. The total amount of scandia in the washings and precipitate amounted to 4·560 grs., which, added to the 0·414 in the solution, makes 4·974 grs. of scandia. The 17·717 grs. of scandium sulphate contain theoretically 4·981 grs. of scandia, so these results are well within experimental errors.

Scandium Selenate.

$Sc_2(SeO_4)_3,8H_2O$.

Dilute and warm selenic acid easily dissolves scandium hydrate or carbonate, and on evaporating the acid solution over sulphuric acid the selenate crystallises in well-defined rhombic prisms, bright, colourless, and capable of withstanding a temperature of 400° without decomposition, except loss of water.

When heated to 100° for sixteen hours, the 8-hydrate oses 6 molecules of water, and becomes a 2-hydrate,—

$Sc_2(SeO_4)_3,2H_2O$.

Analysis.

1. 16·847 grs. of crystallised scandium selenate, heated to 400°, lost 3·709 grs. of water.
2. 16·847 grs. of the same salt gave on ignition to a full yellow heat 3·485 grs. of scandia, = 2·257 grs. of scandium.
3. 13·913 grs. of the crystallised salt, heated to 100° for sixteen hours, lost 2·293 grs. of water.

	Theory.			Experiment.	
				1, 2.	3.
Sc_2 ..	88·200	13·33		13·39	—
$3SeO_4$.	429·600	64·90		64·60	—
$6H_2O$..	108·096	16·33	21·77	22·01	16·48
$2H_2O$..	36·032	5·44			—
	661·928	100·00		100·00	

The anhydrous selenate, heated to a full yellow heat, loses all the selenic acid, and scandia remains.

Analysis.

13·138 grs. of anhydrous selenate left 3·485 grs. of scandia, = 2·257 grs. of scandium.

	Theory.		Experiment.
Sc_2	88·2	17·03	17·18
$3SeO_4$	429·6	82·97	82·82
	517·8	100·00	100·00

Scandium Nitrate, $Sc(NO_3)_3,4H_2O$.

When hydrated, scandia easily dissolves in dilute nitric acid; after ignition it dissolves with the aid of heat in moderately strong nitric acid. The salt is very soluble in water and in alcohol, and is extremely deliquescent. The acid solution, over sulphuric acid, dries up to a viscous gummy mass, in which appear groups of stellate crystals. A neutral aqueous solution evaporated on the water-bath, on cooling, deposits colourless prismatic crystals.

Scandium nitrate decomposes more easily by heat than the nitrate of any other of the rare earths. The crystals deposited from an almost neutral solution get pasty at 100°, but do not run to liquid. In vacuum at 100° the crystals give off water, and frit together, but do not become liquid. Dried on a water-bath, and heated in a tube immersed in melted paraffin with a thermometer by its side, they show signs of melting at 125°. They commence to liquefy at 150°, and when stirred with a platinum wire the crystals run together and form an opaque white liquid.

When scandium nitrate is partly decomposed by heat, and the melted mass extracted with hot water and well boiled, a basic nitrate then deposits, which is difficult to filter owing to its clogging fineness.

The hydrated nitrate, gradually heated in a silica crucible, fuses and boils, becomes opaque and evolves much water. If the heating is stopped at the proper time, the anhydrous nitrate is left, the whole of the water having been driven off. On continuing the heat nitrous vapours come off, and the liquid becomes clear and liquid like water. Increasing the heat turns the liquid brown, and drives off more nitrous vapours, ebullition becomes sluggish,

the fused mass gets white and opaque, and finally there remains a white residue of scandia.

For analysis the nitrate was thrice re-crystallised and repeatedly dried between blotting-paper.

Analysis.

1. 11·136 grs., gradually heated to full redness, left 2·537 grs. of scandia, = 1·6429 grs. of scandium.
2. 25·978 grs. left 5·914 grs. of scandia, = 3·8297 grs. of scandium.

	Theory.		Experiment.	
			1.	2.
Sc	44·100	14·59	14·75	14·74
$3(NO_3)$ .. $4H_2O$ ..	258·094	85·41	85·25	85·26
	302·194	100·00	100·00	100·00

When the above hydrate is dried over a water-bath, it does not fuse, but becomes pasty and anhydrous—

$$Sc(NO_3)_3.$$

Analysis.

1. 38·795 grs. left on ignition 11·449 grs. of scandia, = 7·4141 grs. of scandium.
2. 11·026 grs. of nitrate left on ignition 3·233 grs. of scandia, = 2·0936 grs. of scandium.
3. 14·618 grs. of nitrate left on ignition 4·287 grs. of scandia, = 2·7762 grs. of scandium.

Synthesis.

4. 4·246 grs. of ignited scandia (= 2·7496 grs. of scandium) were covered in a crucible with strong nitric acid and put into a hot oven at 100° for seven hours. All excess of nitric acid disappeared, and a clear oily liquid remained which solidified on cooling. No crystals were seen, but the substance resembled glass. The solid nitrate weighed 14·008 grs.
5. 3·233 grs. of scandia (= 2·0936 grs. of scandium), treated as described in the last experiment, formed 11·026 grs. of nitrate.

	Theory.		Experiment.				
			1.	2.	3.	4.	5.
Sc ..	44·10	19·16	19·11	18·99	18·99	19·63	18·99
$3(NO_3)$	186·03	80·84	80·89	81·01	81·01	80·37	81·01
	230·13	100·00	100·00	100·00	100·00	100·00	100·00

When the hydrated nitrate is dried *in vacuo* at 100° for seventeen hours it becomes a basic nitrate—

$$ScOH(NO_3)_2,H_2O.$$

Analysis.

21·679 grs. of this basic nitrate lost on ignition 14·475 grs., and left 7·204 grs. of scandia, = 4·665 grs. of scandium.

	Theory.		Experiment.
Sc	44·100	21·71	21·52
OH .. .. $(NO_3)_2$ .. .. H_2O	159·044	78·29	78·48
	203 144	100·00	100·00

Therefore the nitrate has lost one equivalent of nitric acid.

When the nitrate is heated for twelve hours in a hot-air oven at a temperature of 120°, a basic nitrate is left of the composition—

$$Sc_2O(NO_3)_4.$$

Analysis.

1. 6·550 grs. left on ignition 2·537 grs. of scandia, = 1·6429 grs. of scandium.
2. 13·698 grs. left on ignition 5·287 grs. of scandia, = 3·4237 grs. of scandium.

	Theory.		Experiment.	
			1.	2.
2Sc	88·20	25·04	25·08	24·99
O .. .. $4(NO_3)$ ..	264·04	74·96	74·92	75·01
	352·24	100·00	100·00	100·00

SCANDIUM FORMATE,

$$(HCOO)_2ScOH,H_2O.$$

Scandium hydroxide dissolves readily in formic acid. The solution is evaporated to expel excess of acid and dissolved in water. It is then allowed to evaporate over sulphuric acid in a desiccator, when it forms hard and lustrous crystals, easily soluble in hot water and in alcohol.

The formate readily decomposes when heated, and at a red heat leaves a white residue of scandia.

Analysis.

8·895 grs. of crystallised formate left on ignition 3·650 grs. of scandia, = 2·363 grs. of scandium.

	Theory.		Experimen
Sc	44·10	26·07	26·57
$(HCOO)_2$ .. .. OH .. .. .. H_2O..	125·04	73·93	73·43
	169·14	100·00	100·00

(To be continued).

THE ACTION OF CHLORINE UPON UREA WHEREBY A DICHLORO UREA IS PRODUCED.*

By FREDERICK DANIEL CHATTAWAY, F.R.S.

ALTHOUGH a few of the more familiar substances containing halogen attached to nitrogen, as, for example, nitrogen chloride, have been known for a long period, it is only within the last ten years that such compounds have been systematically studied. They form, however, a group of extraordinary interest, and play an all-important part in many complex reactions; to illustrate this it is only necessary to refer to the substitution of halogen in anilides and to the well-known method for obtaining amines from amides. I have shown in a series of investigations that hydrogen attached to nitrogen in compounds of the most varied characters may be replaced with ease by chlorine or bromine if suitable conditions are observed, and it may be said, speaking generally, that this can always be done, although the nitrogen halogen derivatives produced may react or undergo isomeric change so readily that they can only with difficulty be isolated.

All compounds in which halogen is directly attached to trivalent nitrogen can take part in certain well-defined reactions characteristic of the linkage. One of the most striking of these group reactions is that with hydriodic acid, whereby at the ordinary temperature the halogen is replaced by hydrogen and iodine is liberated quantitatively. This reaction, which may be expressed by the general equation $:NX+2HI=:NH+HX+I_2$, affords an easy method of analysing these compounds.

Such a nitrogen halogen derivative is formed as an intermediate product in a reaction with urea, the course of which has never hitherto been explained although it has

* A Paper read before the Royal Society, June 25, 1908.

received an unusual amount of attention on account of its furnishing a ready method of estimating the quantity of this substance present in a liquid.

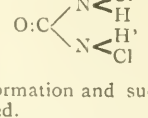
When urea is added to a solution of an alkaline hypochlorite or hypobromite it is at once decomposed, nitrogen and carbon dioxide being set free; if an excess of alkali is used the carbon dioxide is fixed, and the nitrogen, which alone escapes, should thus afford a measure of the amount of urea. The reaction is generally represented by the equation $CO(NH_2)_2+3NaOBr = CO_2 + N_2+3NaBr+2H_2O$. which throws no light upon its nature; indeed, it obscures it, as it makes it appear to be a case of oxidation. It does not even express quantitatively what takes place, for all chemists who have investigated the decomposition have noted that the amount of nitrogen liberated is invariably less than that contained in the urea used. When the operations are carried out under specified conditions this loss of nitrogen, which may amount to as much as half of the total, is very constant, and so can be allowed for by adding a definite fraction of the whole to the gas actually measured. The method can thus be made to give results sufficiently accurate for clinical purposes, and since it is easy to carry out it has received very general application. It is not known what becomes of the nitrogen which does not appear as gas, for all the suggestions that have been made hitherto wholly fail to account for more than a small fraction of the quantity that disappears.

If urea be added instead of to an alkaline solution of a hypochlorite to one acidified by acetic acid, that is to a solution of hypochlorous acid, no gas is evolved, nor is any gas liberated if chlorine itself is passed into a solution of urea in acetic acid. Action, however, takes place in each case, and a nitrogen chloride is produced; for although the hypochlorous acid or chlorine disappears, the resulting solution liberates iodine in large quantity from hydriodic acid.

The isolation of the substance produced from such a solution is not practicable, since the method of extraction by chloroform which often serves for the separation of substituted nitrogen chlorides cannot be used, as the chloro urea formed is easily soluble in water but almost insoluble in chloroform. It is, however, less soluble in water than urea itself, and crystallises out in a pure condition when chlorine in excess is passed rapidly through a cooled sufficiently strong aqueous solution of urea. The action which takes place is represented by the equation $CO<^{NH_2}_{NH_2} + 2Cl_2 = CO<^{NHCl}_{NHCl} + 2HCl$, two only of the four hydrogen atoms of the urea being replaced by chlorine.

This dichloro derivative appears to be the only stable nitrogen chloride which urea is capable of forming. The crystals which separate from the solution of urea have this composition from the first, and chlorine seems to have no further substituting action upon them.

Dichloro urea, having regard to its mode of formation, as well as to the structure of urea itself, has most probably the constitution represented by the formula—



which explains its formation and such of its reactions as have yet been studied.

If this constitution be granted it seems probable that the reaction between urea and chlorine takes place in two stages, and that the amino groups are substituted successively, but the monochloro derivative does not crystallise out, possibly owing to its solubility being not far removed from that of urea itself. Either of two causes may prevent the formation of a ter- or tetrachloro derivative; the hydrochloric acid which is formed in the reaction may prevent that addition of chlorine to the nitrogen which must precede further substitution, or the more highly substituted urea may be hydrolysed so easily that it breaks up as soon as it is formed. Dichloro urea is so much more easily hydrolysed than urea itself that the latter is the more probable cause.

Although two molecules of hydrogen chloride are formed when urea is substituted by chlorine, very little heat is developed; dichloro urea must therefore be an endothermic compound, and might be expected to be highly explosive. When heated, however, it does not explode itself, but decomposes with liberation of nitrogen chloride, which, if heated a few degrees above the temperature at which it is set free, may detonate with great violence.

Dichloro urea gives all the characteristic reactions of a typical nitrogen chloride; for instance, it liberates iodine from hydriodic acid, chlorine from hydrochloric acid, and reacts with alcohol, forming ethyl hypochlorite, urea being in each case re-formed.

It is distinguished from most other substituted nitrogen chlorides by the readiness with which it is hydrolysed in presence of water, nitrogen chloride, carbon dioxide, a little nitrogen and ammonium chloride being formed. If the compound is dissolved in water or kept in a moist atmosphere, this hydrolysis takes place slowly at the ordinary temperature, and becomes very rapid at about 30° C.

It is probable that in this reaction a mono-substituted ammonia is first produced, thus:—

$$CO<^{NHCl}_{NHCl} + 2H_2O = CO<^{OH}_{OH} + 2NH_2Cl;$$

but if so it apparently can only exist momentarily, as nitrogen chloride is at once liberated. The formation of the end products of the reaction can be explained by assuming that this monochloro ammonia at once breaks up into ammonia and nitrogen chloride, $3NH_2Cl = 2NH_3 + NCl_3$, which then to some extent react, forming nitrogen and hydrogen chloride, the latter at once combining with the free ammonia and allowing the remaining nitrogen chloride to escape, as this does not react with ammonium chloride. Both acids and alkalis accelerate the rate of hydrolysis, and also alter the nature of the end products by hindering or furthering the secondary reaction between the ammonia and the nitrogen chloride.

In the presence of dilute acids the ammonia is at once fixed, and the reaction between it and the nitrogen chloride with its accompanying liberation of nitrogen is prevented; all the chlorine contained in the dichloro urea is therefore liberated as nitrogen chloride. In presence of alkalis, on the other hand, the reaction between the ammonia and the nitrogen chloride goes on to completion, since the hydrochloric acid formed in it is at once fixed; no nitrogen chloride therefore is set free, since twice as much ammonia is formed as is required to decompose it.

The reaction between dichloro urea and a solution of caustic potash is instantaneous; nitrogen is liberated with violent effervescence, the excess of ammonia and the alkaline carbonate formed remaining dissolved in the liquid. The action, which is quantitative, is expressed by the equation—

$$3CO<^{NHCl}_{NHCl} + 12KOH =$$
$$= 3K_2CO_3 + 2NH_3 + 6KCl + 2N_2 + 6H_2O.$$

The behaviour of dichloro urea with alkalis affords an explanation of the course of the reaction which occurs when urea is decomposed either by an excess of alkaline hypochlorite or hypobromite. The urea, is, without doubt, converted into dichloro or dibromo urea (see Note), which is at once hydrolysed in the manner above described. In presence of the excess of hypochlorite or hypobromite, the mono-substituted ammonia formed in the hydrolysis may be further substituted to a greater or less extent, nitrogen being evolved quantitatively only when this takes place under such conditions that the amount of hydrogen attached to nitrogen in the reacting system is always sufficient to react completely with the chlorine attached to nitrogen.

NOTE.—It is possible that in absence of free acid, and

in presence of excess of hypochlorite or hypobromite, a tri- or tetra-substitution product may be produced, the formation and decomposition of which can be formulated easily, but this does not affect the essential character of the reaction, which is one of halogen substitution followed by hydrolysis of the substituted urea and interaction between the resulting compounds.

Preparation of Dichloro Urea.—The preparation of dichloro urea should be carried out at a low temperature and as rapidly as possible, since, in presence of the hydrochloric acid formed at the same time, hydrolysis so readily occurs and so much nitrogen chloride is produced that if it is carried out at the ordinary temperature, or its duration is unnecessarily prolonged, a poor yield is obtained. It is best therefore to work with small quantities, to cool thoroughly, and to pass the chlorine as rapidly as possible. The following procedure gives a good result:—Dissolve 20 grms. of urea in 40 cc. of water, and cool to about −10° C. in a mixture of alcohol and crushed ice. (It is not absolutely necessary to use a freezing mixture, the temperature, owing to the urea dissolving, falls at once to below zero, and if the flask in which the operation is carried out is cooled by tap-water, a moderate amount of the compound can be obtained, but the yield is much better at a lower temperature). Pass in as rapidly as practicable a stream of chlorine made by dropping strong hydrochloric acid upon bleaching-powder. So little heat is evolved in the reaction that with proper cooling the temperature never rises above zero, however rapid the stream of chlorine. Nitrogen chloride is produced from the first, and can be recognised by its characteristic smell, but it remains in solution, the liquid, owing to its presence, becoming bright yellow in colour. After passing the chlorine for a considerable time, white crystals make their appearance, at first usually on the surface of the liquid; these increase in amount till the whole becomes a pulp of thin colourless plates. When these no longer appear to increase in amount, filter off, separating the acid mother-liquor as completely as possible; wash once or twice with a little water, and when as much of the latter as possible has been removed wash the crystals several times with dry chloroform. Dichloro urea is not appreciably soluble in cold chloroform and a good deal of adhering moisture is thus got rid of. Press finally between filter-paper, spread out in a thin layer on a clock glass, and free from the last traces of water by exposing for about half-an-hour over phosphoric oxide in a vacuum.

A further crop of crystals can be obtained by again passing chlorine through the cooled mother-liquor, and this can be repeated as long as any separate. Nothing besides dichloro urea and the products of its hydrolysis are formed in the reaction; if the acid mother-liquor is evaporated down, carbon dioxide is given off and nitrogen chloride escapes in quantity; later, as the liquid becomes concentrated, hydrogen chloride is expelled, and finally ammonium chloride is left.

Although the final result of the action which takes place is the substitution of two atoms of hydrogen by two atoms of chlorine, as in other similar cases, this is without doubt effected by the addition of four atoms of chlorine to the nitrogen followed by the elimination of two molecules of hydrogen chloride.

Ths yield of dichloro urea is not very large, so much being hydrolysed during the process; in a well conducted experiment it reaches about 25 per cent of the theoretical, the weight of pure dry product obtained amounting as a rule to rather more than half the weight of the urea used. The loss, although largely due to the hydrolysis of the compound, is much increased by the circumstance that dichloro urea is very soluble in water, and consequently a considerable amount does not crystallise out from the mother-liquor.

Dichloro urea reacts with an aqueous solution of hydriodic acid in the way characteristic of nitrogen chlorides; urea is reformed and iodine quantitatively liberated. It was analysed by taking advantage of this reaction; a known weight was added to an excess of a solution of potassium iodide made acid by acetic acid and the iodine liberated estimated by a standard solution of sodium thiosulphate.

0·5112 grm. liberated iodine = 158·6 cc. N/10 I. Cl, as :NCl = 54·99 per cent. $CON_2H_2Cl_2$ requires Cl, as :NCl = 54·96 per cent.

Dichloro urea cannot be kept for any length of time without change. When damp it hydrolyses exactly as when dissolved in water. To obtain it pure, therefore, it must be dried very rapidly over phosphoric oxide in a vacuum. When only freed from adhering water as far as possible by a pump, it is slowly hydrolysed by the retained moisture even though placed in a desiccator over strong sulphuric acid, and this often occurs to such an extent that the mass becomes quite yellow from the nitrogen chloride mechanically retained by the crystals. To show the amount of hydrolysis which takes place under these conditions a quantity of the pure substance freed from all but adhering water thus was kept over strong sulphuric acid, and analysed from time to time, the nitrogen chloride formed being allowed occasionally to escape. In two days the percentage of chlorine as :NCl had fallen to 43·79, and in seven days to 13·33.

Even when dried and kept over phosphoric oxide it slowly decomposes, nitrogen chloride being evolved. A quantity of the pure dry compound thus preserved in a vacuum over phosphoric oxide was analysed at intervals; after twelve hours the percentage of Cl as :NCl had fallen to 54·67, after two days to 52·97, and after nine days to 47·87 per cent.

When an aqueous solution is kept at the ordinary temperature the dichloro urea is slowly hydrolysed; carbon dioxide, a little nitrogen, and nitrogen chloride escaped, and ammonium chloride remains in solution. Hydrolysis by water takes many days to complete unless the aqueous solution is warmed, when it is much more rapid; at about 20° bubbles of gas are freely evolved and rapid effervesence sets in at about 40°, the nitrogen chloride escaping without explosion.

Dichloro urea prepared as described above is a soft white crystalline powder with a pearly lustre. Under the microscope it is seen to consist of thin transparent plates somewhat irregular in shape. It can be re-crystallised from water, in which it is easily soluble and from which it separates in similar but larger plates, by cooling an aqueous solution saturated at about 15° C., though with some loss owing to hydrolysis. Its aqueous solution is at first colourless but becomes yellow as hydrolysis proceeds, owing to the liberation of yellow nitrogen chloride which remains dissolved in the water. It is easily soluble in alcohol and ether, very slightly soluble in chloroform, and insoluble in petroleum ether. When its alcoholic solution is heated it reacts in the way characteristic of nitrogen chlorides, urea is reformed, and ethyl hypochlorite is produced, the latter very easily breaking down into aldehyde and hydrogen chloride.

Its behaviour with acids is complicated by the circumstance that it is so readily hydrolysed; for example, when it is added to strong hydrochloric acid, though chlorine is rapidly given off the amount of urea reformed is not very large. When placed in cold strong sulphuric acid it is hydrolysed and nitrogen chloride is liberated. The latter decomposes into its elements if the liquid be heated, its characteristic smell disappearing and being replaced by that of chlorine.

Dichloro urea is a compound of a marked acid character, it has an acid taste recalling that of hypochlorous acid and its aqueous solution strongly reddens litmus-paper, which only becomes bleached after the lapse of some minutes. It acts very corrosively upon the skin, staining it yellow and destroying the tissues.

When heated, dichloro urea melts with decomposition at about 83°, nitrogen chloride being liberated. Although the substance appears not itself to explode, if the temperature

of the bath in which the melting-point is being taken is allowed to rise at all rapidly a few degrees above this point, the nitrogen chloride set free in the melting-point tube may explode with considerable violence.

It can be decomposed without danger by throwing it into a porcelain dish heated to 100° on a water-bath in quantities of not more than about half a grm. at a time. The white compound fuses and gives off nitrogen chloride as a yellow vapour which escapes quietly unless, through too large a quantity of material having been decomposed at once, some of the vapour is mechanically retained as bubbles in the semi-fused residue, and thus becomes heated to the temperature at which it explodes. Hydrogen chloride is not set free when dichloro urea is thus decomposed by heat.

When an aqueous solution of the compound is added to a solution of caustic soda, vigorous effervescence, due to escape of nitrogen, occurs. The liquid remaining contains ammonia and potassium carbonate, the volume of carbon dioxide liberated when this is treated with an acid being to the volume of nitrogen previously liberated in the ratio of 3 to 2. One-third of the nitrogen contained in the dichloro urea used is found as ammonia.

The investigation of dichloro urea, which is an extremely reactive body and promises to be of considerable use in organic synthesis, is being continued.

The thanks of the author are due to Dr. Baker for allowing him to use the Christ Church Laboratory, where this work has been carried out.

NOTE ON

THE FORMATION OF FORMALDEHYDE IN SOLUTIONS OF CANE-SUGAR, AND ITS BEARING ON HEHNER'S TEST FOR FORMALDEHYDE IN SACCHARIN MIXTURES.

By A. ALEXANDER RAMSAY.

Trillat has shown that on heating cane-sugar, traces of formaldehyde are given off even at 125° C. ("The Formation of Formaldehyde in the Caramelisation of Sugar," *Bull. Soc. Chim.*, 1906, xxv., 681). At 150° C. the aldehyde is liberated in greater quantity. Analysis of the vapours emitted at 200° C. showed the presence of 0·2 to 5·7 per cent formaldehyde, and the residual caramel contained up to 0·27 per cent of polymerised formaldehyde, probably in the state of trioxymethylene. The amounts produced were found to vary with the method of heating, the nature of the vessel, and the purity of the sugar.

The object of the present note is to draw attention to the fact that the production of formaldehyde takes place in minute quantities when cane-sugar and water are heated together from 100—103° C. This fact renders the Hehner test (*Analyst*, 1896, xxi., 95) unreliable as an indication of the addition of formalin to jam or saccharin beverages, since formaldehyde is produced in the manufacture of jam. Moreover, the act of distilling a saccharin liquid results in the formation of formaldehyde, even if it were not originally present.

The following experiments were performed :—

1. 100 grms. pure cane-sugar was dissolved in 5 ozs. cold distilled water, heated for half an hour, and distilled. The distillate gave the reaction for formaldehyde with Hehner's test (*loc. cit.*). The boiling-point of the residue in the retort was 103° C.

2. 50 grms. pure cane-sugar was dissolved in 5 ozs. cold distilled water in a glass retort and heated till the mixture boiled, and distilled. The distillate which was obtained during the first twenty minutes was collected and marked *a*. The receiver was changed, and the distillation continued for about twenty minutes longer, the distillate collected and marked *b*. The liquid remaining in the retort was diluted with cold distilled water to 5 ozs., and again heated and distilled—collecting the distillate separately and marking it *c*. When the distillation was finished the sugar solution in the glass retort was crystal clear, had no yellow tinge, boiled at 101—101·5° C., and gave a strong reaction for formalin.

The three portions of distillates marked *a*, *b*, *c* were tested for formaldehyde by Hehner's test, and all gave the reaction, though faintly. The remainder of portion marked *a* was re-distilled, and the first 5 cc. caught and marked *a'*. This gave a strong reaction for formaldehyde both by Hehner's test and Pilhastry's test (Cohn, "Tests and Reagents").

The remaining portions of distillate marked *b* and *c* were similarly treated, the first 5 cc. of each caught and marked *b' c'* respectively. Both *b'* and *c'* gave the Hehner reaction for formalin, *c'* less strongly than *a'* or *b'*.

The foregoing taken with Trillat's note, explains the occurrence of formaldehyde in jam made from pure fruit, cane-sugar, and water. Jam was prepared from pure fruit and pure cane-sugar as follows :—

Peach.—1 lb. fruit, 1 lb. sugar, 3½ ozs. water, boiled about two hours.

Orange.—1 lb. fruit, 2 lbs. sugar, 13 pints water, boiled about two hours.

Quince.—1 lb. fruit, ¾ lb. sugar, 1 pint water, boiled about two hours.

Quince Jelly.—1 lb. fruit, 1 lb. sugar, 1 pint water, boiled about two hours.

Unfortunately at the time these jams were prepared the boiling-points of the various mixtures was not noted. The temperature was certainly never above that reached in making jam on the manufacturing scale, and there was no possibility of caramelisation.

On examining the foregoing four jams for formalin (by distilling a portion faintly acidified and testing the distillate) reactions were obtained in all cases—in the case of the orange jam the reaction was particularly strong.

Further investigation as to the amounts of formaldehyde present are being carried out, and the results will be embodied in a future paper. The experiment also shows the unsuitability of the method of examining jams for formaldehyde, by dissolving 50 grms. sample in 250 cc. water as recommended by Leach ("Food Inspection and Analyses"), acidifying with phosphoric acid, distilling, and testing the first 30 cc. distillate for formalin. After 125 cc. distillate has been obtained, further distillation yields a distillate containing still larger quantities of the aldehyde.

The presence of formaldehyde in various foods has been noted by Perrier ("Presence of Formalin in Certain Foods," *Comptes Rendus*, 1906, cxliii., 600),, who finds in cider 0·2 to 0·33 parts formaldehyde per 100,000, and in bacon, ham, sausage, herring, &c., amounts varying from 0·03 to 0·003 parts per 100,000. In jams examined by the author the amounts of formaldehyde have varied from 1·3 to 14 parts per 100,000.

Experiment 2 mentioned previously was repeated with the object of applying other confirmatory tests for the formaldehyde present, by the Gayon-Saglien-Mohler reagent (M. X. Rocques, "Analysis of Alcohol and Brandy," *Rev. Internat. de fals. and d'Anal. des Matieres Alimentaires*, April, 1907, p. 49), Pilhastry's reagent (Cohn, "Tests and Reagents"), Hehner—aqueous phenol (*Ibid.*, p. 121), and Hehner—commercial sulphuric acid (*Ibid.*, p. 121). Reactions clear and well defined were obtained by both Hehner's tests and a faint reaction with Pilhastry's reagent, but no reaction with the Gayon-Saglien-Mohler reagent.

While carrying out these tests I found Hehner's milk-sulphuric acid test most delicate; 1 part formalin in four millions gave a clear reaction in two minutes, and up to 1 in ten million on standing a little longer, provided the milk is added to the solution of formaldehyde immediately before the addition of the sulphuric acid. The aqueous phenol and sulphuric acid reacted up to 1 part in four millions. Pilhastry's reagent seems to detect only 1 part

in half a million, and the Gayon-Saglien-Mohler reagent about 1 part in a quarter of a million.

It has also been shown by Forster that furfuraldehyde is produced in small quantities by boiling sugar with water (*Ber.*, xv., 230), but in the experiments detailed above I find no furfural reaction, only formaldehyde. In the case of furfural in dilute aqueous solution with Hehner's test (milk-sulphuric acid), at the junction of the two liquids a faint pink zone is formed, which darkens, forming a decided green colour which deepens on standing. With Hehner's aqueous phenol and sulphuric acid test applied to furfural, a purple black band forms at junction of the liquids which deepens in colour on standing and increases in size. These reactions are quite dissimilar to the reactions of formaldehyde.—*Journal and Proceedings of the Royal Society of N. S. Wales*, vol. xli., p. 172.

THE PRESENT STATE OF OUR KNOWLEDGE OF RADIO-ACTIVITY.*

By A. DEBIERNE.

(Continued from p. 273).

II.

It will be observed that though the numbers obtained for thorium and uranium are very large and comparable with the intervals of time reckoned in geological transformations, the life of radium, on the contrary, is comparatively short; its existence on the earth's surface could not be explained unless the destruction of it was compensated by a continuous production, and this production must take place at the expense of the substances which accompany it in minerals. The fact, proved in Mdme. Curie's first experiments, that only minerals which contain uranium or thorium are appreciably radio-active, and the fact that radium is extracted from uranium minerals, lead us to suppose that it is uranium which produces radium, and that in radio-active transformations the radium series is a continuation of the uranium series.

Researches on the radio-active minerals have disclosed an important argument in favour of this view. Boltwood has determined the amount of uranium in a large number of radio-active minerals obtained from various places in Europe and America, and at the same time he has measured the ionisation produced at the end of three hours in a given container by the emanation set free by these minerals when they are dissolved in an acid.

As, up to the present, radium emanation is the only emanation known which has a fairly long life, there is reason for thinking that it alone exists in gases extracted from minerals some hours after extraction. Moreover, the ionisation produced in the same container by the emanation set free by a given quantity of radium has been determined, and hence the proportion of radium contained in the minerals could easily be calculated. Applying various corrections for the liberation of emanation by the minerals before they were treated, Boltwood found that the ratio between the quantity of radium and of uranium is a constant for all uranium minerals. This result is confirmed by the experiments of McCoy and Eve, in which the intensity of the radiation of the minerals was measured, taking into account certain peculiarities of the radiation of radium. Thus the methods of determining radium are indirect, but the agreement of the results is such that it is difficult to entertain any doubts concerning the actual existence of this constant ratio of radium to uranium in minerals. (However, Danne has shown that certain pyromorphites containing considerable amounts of radium do not contain uranium, but this anomaly can easily be explained as a chemical separation effected by the action of water).

This fact, which in itself indicates a connection between radium and uranium, may be explained as follows:—

If radium is produced by uranium, and if the destruction of radium is rapid compared to that of uranium, it is easy to see that the quantity of radium in equilibrium is directly proportional to the quantity produced by the uranium in a given time; that is to say, to the total quantity of uranium. It must thus be supposed that uranium has a very slow rate of decay, in order to explain its presence on the surface of the earth. Other considerations point to a life of 5×10^9 years.

If the production of radium from uranium were direct, according to the above data, the phenomenon would be of sufficient magnitude to be established directly by experiment.

Different experiments have been arranged by Soddy. He first obtained a positive result which, however, was much smaller than that foretold by theory; his later experiments gave so low a result that it might be due to experimental errors; in fact, up to the present time the formation of radium by uranium has not been proved by direct experiment.

To explain this result and yet ascribe to radium the relatively short life, demanded in accordance with Rutherford's hypotheses, it may be supposed that radium is not the direct product of uranium. Then if an intermediate term exists, having a very long mean duration of life, the formation of radium from pure uranium could not be proved until a large enough quantity of this intermediate product had been formed and destroyed; this would explain the negative result of the experiments on the direct formation of radium from uranium.

Recent experiments by Rutherford and Boltwood verify this supposition. Some time ago I showed that compounds of actinium always liberate very small quantities of an emanation with a slow rate of decay, which I afterwards found to be radium emanation; thus actinium might be supposed to be the intermediate substance. Boltwood and Rutherford first thought this; moreover, they proved a slow increase in the quantity of radium emanation in certain specimens of actinium. However, they recognised that this production of emanation, which apparently involves that of radium, is due to a substance differing from actinium and accompanying it in fairly large quantities in the specimens used by Rutherford and Boltwood. This new substance, which has been prepared only in a very dilute state, Boltwood called ionium. (The proportion of radium emanation, liberated by my specimens of actinium, is much less than the proportion found by Rutherford in a specimen obtained from Giesel). Thus, summarising, we may say that if the direct production has not been shown experimentally the succession is very probable, and the negative result can easily be explained.

According to these experiments, uranium and radium would form a single series; but, as far as we know, thorium and actinium would form separate series, unrelated to one another and to the other series.

III.

Radio-active transformations may be accompanied by different secondary phenomena. We have already seen that the rays emitted by radio-active substances produce the phenomena of ionisation, phosphorescence, and photographic action. Chemical actions have also been demonstrated. The first action to be observed was the transformation of oxygen into ozone under the influence of radium emanation (Pierre Curie and Mdme. Curie). By the action of the radiation from radium, white phosphorus is transformed into red phosphorus, iodine is set free from iodic acid, &c.

The most remarkable chemical action is the decomposition of water into hydrogen and oxygen; it was first observed by Giesel with radium solutions; with a solution containing 1 decigrm. of radium bromide little bubbles of gas can easily be seen forming continuously in the midst of the solution. Ramsay in recent experiments obtained the same decomposition by the action of radium emanation; he also proved that the quantity of oxygen obtained is smaller than that corresponding to the formula $H_2 + O$.

* *Revue Générale des Sciences.* 1908, xix., 730.

I observed that actinium solutions exhibit the same phenomenon, and that the liberation of gas in a solution is perfectly regular and proportional to the time In recent experiments, which have not yet been published, I have found that the decomposition of water is due only to the penetrating radium rays. This is a very interesting result, for I think it is the first time that such a reaction has been caused by the action of a radiation.

The rays of radio-active substances and particularly those of radium have the power of colouring certain substances, glass, porcelain, alkaline salts, barium platinocyanide, fluorspars, quartz, diamond, &c. These colorations, which may be very intense, seem to be the same as those which are caused by the cathode rays. Many hypotheses concerning the nature of these colorations have been suggested, but very little is actually known about them. By the action of cathode rays on common salt metallic sodium is formed in the mass, and can be separated by distillation; hence it has been suggested that the colorations may be due to the presence of metallic particles. However, I think that the colorations cannot generally be due to metallic particles, and that the reaction must occur in two stages, the first being analogous to that observed with silver salts on a photographic plate, before they are reduced to the state of metallic silver.

I have suggested a theory in which these coloration phenomena are connected with the phenomena of phosphorescence and thermoluminescence; it may be mentioned that the presence of very small quantities of impurities has a marked influence on the nature of the coloration, and this is to be ascribed to the influence of the impurities on the phenomena of phosphorescence.

Chemical actions under the influence of radio-active transformations have been but little studied; it seems, however, very probable that they are very frequently produced, either by the action of the rays or of the centres of radio-activity. Mdme. Curie, who showed some time ago that the condensation of gases is produced in presence of the emanation, has observed that these phenomena are accompanied by chemical reactions. Probably radio-active substances are very energetic agents in producing chemical reactions, but the small quantities dealt with render the study of the subject very difficult.

Recent experiments by Ramsay and Cameron go to show that much more energetic actions may be induced by the aid of radio-active substances. In fact these investigators have reported that under the influence of radium emanation ordinary elements may be dissociated and transformed into other elements. The experiments are as follows:—If large quantities of radium emanation are allowed to act on distilled water, besides the oxygen and hydrogen resulting from the decomposition of the water, a small quantity of neon is obtained in place of the helium which was formed in previous experiments with the dry emanation. When this emanation is allowed to act on a solution of a copper salt the gas obtained is argon; moreover, in the solution, after the separation of the copper, an appreciable amount of sodium and potassium salts and a small quantity of lithium salts can be detected. In control experiments performed without emanation or without copper salts so large a quantity of alkaline salts was not obtained, nor was the presence of lithium detected.

Ramsay concludes from these experiments that copper undergoes a disintegration under the action of the emanation, and that potassium, sodium, and lithium are the products of this disintegration.

These results are too important to be accepted without a rigorous experimental proof, and it must be noted that such a demonstration is extremely difficult in the present case. As a matter of fact, these experiments are far less conclusive than those which show the formation of helium by radium. For the element helium does not exist in the air nor in the substances which are present during the experiments. In many blank experiments performed in absence of radium under different conditions, I have never observed the formation of helium. The brilliant and very characteristic spectrum of this element makes it quite easy to detect its formation with certainty; finally, in my experiments I have been able to establish an almost perfect proportionality between the duration of the action of the radium and the amount of helium obtained. Thus many experiments have confirmed the discovery of Ramsay and Soddy, and Giesel has recently confirmed my experiments on the formation of helium by actinium.

On the contrary, in Ramsay and Cameron's recent experiments the elements, which have been obtained by the action of radium emanation are among those which might have been accidentally introduced in the course of the different operations. Neon and more particularly argon are contained in appreciable amounts in air, and a trace of air left in the apparatus might be revealed at the end of the experiment by the presence of these gases, for oxygen is absorbed in the manipulations, and nitrogen might also be eliminated by combining with oxygen under the influence of the emanation. In confirmatory experiments which I performed I always obtained only a small quantity of argon (moreover, this quantity is much smaller than the quantity of helium formed by radium or actinium).

In the experiments with copper salts, as Ramsay himself pointed out, the presence of sodium and potassium might be due to an action on the glass apparatus which was used in the experiments; but we have seen that the proportion of these elements is considerably greater than in the blank experiments, carried out either with the emanation alone or with the copper salt alone. It is not impossible to imagine that the glass of the vessels is rendered peculiarly liable to attack by the simultaneous presence of the emanation, with all the radiations which accompany its destruction, and which may produce a pulverisation of the glass and of the acid solutions of the copper salts.

At first sight it would seem much easier to demonstrate the production of lithium. However, the quantity obtained is much smaller than that of the compounds of sodium and potassium, about 1/10,000 according to Ramsay and Cameron's statements, and the suggestion that the glass it attacked is still feasible; for although an appreciable amount of lithium in glass has not been detected by analysis, it is not impossible that a proportion of 1/10,000 of lithium might occur in the alkalis of the glass; lithium is known to be very widely distributed in nature, especially in the materials which might be used for the preparation of glass. Finally, the unexpected discovery has been made that lithium is a constant impurity in copper salts, and Ramsay was only able to obtain a copper salt free from lithium with very great difficulty.

The formation of lithium has been the subject of many researches on the radio-active minerals. McCoy in America and Mlle. Gleditsch in the laboratory of Mdme. Curie in France, have found independently that all radio-active minerals contain a small quantity of lithium, and and this result seems at first to be an argument in favour of Ramsay's conclusions. But Mlle. Gleditsch, by determining the lithium and also the copper in active minerals, has proved that the quantity of lithium is very small, and that there is no relation between it and the radio-activity, nor between it and the amount of copper present. In particular the mineral which seemed to fulfil best the conditions for the formation of lithium, chalcolite, a phosphate of uranium and copper, which is strongly radio-active and contains the largest proportion of copper, is also the mineral which contains the least lithium. And even the presence of this small amount of lithium might be attributed to the fact that the mineral might contain a small quantity of gangue which contains an appreciable amount of lithium. As Ramsay has pointed out, this result is not an argument absolutely contrary to the formation of lithium, for the latter might depend upon external circumstances not realised in chalcolite. However, seeing that radio-active transformations appear to be absolutely unaffected by external conditions, it is impossible to conceive what the circumstance could be which would hinder the formation of lithium in chalcolite. The

result of the researches on minerals is thus on the whole unfavourable to the idea of the transformation of copper into lithium under the action of the emanation.

Thus, in spite of Ramsay's great scientific reputation and the confidence which we feel in his skill as an experimenter, and in spite of his discovery of the formation of helium which has been completely confirmed, I think that we must wait for fresh researches before forming a definite opinion concerning these new results.

It is hardly necessary to point out that if these results are confirmed they will be of fundamental importance for the development of chemical science in general and of researches on radio-activity.

In reality these new transformations are entirely different from those which are assumed in radio-active transformations, and also from the production of helium as it is explained according to our present theories. Thus radio-active transformations occur spontaneously, and we cannot by any means whatever start or stop them, nor even exert any influence over the rate at which they occur; we watch this evolution of the elements as powerless spectators who cannot modify it in any way. But in Ramsay's experiments the transmutations were caused artificially by bringing together two elements, emanation and copper, which are capable of reacting, exactly as in any chemical reaction. This marks a very decided progress, and I sincerely hope that it will be realised.

It is also probable that the present theories of radio-activity will undergo some modifications, for if radium emanation causes atomic transmutations in the substances which accompany it, it is conceivable that these substances may intervene in the radio-active transformations, and that the helium, for example, does not come from the radio-active atom but from the substances which may accompany it.

(To be continued).

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

Part III.—Analysis of the Aluminium and Iron Groups, including Beryllium, Uranium, Vanadium, Titanium, Zirconium, and Thallium.

By Arthur A. Noyes, William C. Bray, and Ellwood B. Spear.

(Continued from p. 265).

Confirmatory Experiments and References (continued).

Condition of Vanadic Acid in Solution.—See Düllberg (*Zeit. Physik. Chem.*, 1903, xlv., 129—181). He considers that in a solution of the composition of Na_3VO_4, which reacts strongly alkaline, the salt is largely hydrolysed according to the reaction $2Na_3VO_4 + H_2O = 2NaOH + Na_4V_2O_7$, but his evidence is not convincing. On adding HCl slowly the results indicate the presence of a tetrabasic acid, $H_4V_6O_{17}$. This is a strong acid, two of the hydrogens splitting off nearly completely in dilute solutions, and the third one to a considerable extent. The yellow colour is probably due to the ion $HV_6O_{17}\equiv$. The transition of one form of vanadic acid into another takes place readily, the final equilibrium state being reached fairly quickly. Conductivity and freezing-point determinations make it probable that the formula of sodium metavanadate is $(Na+)_3V_3O_9\equiv$.

*P. 58*b*, N. 1: *Partial Decomposition of* H_2O_2 *in the* $NaHCO_3$ *Treatment.*—A mixture containing 100 mgrms. U as $UO_2(NO_3)_2$ and 100 mgrms. V as Na_3VO_4 was treated by P. 52 and *P. 58*a*, and then was acidified with HNO_3; the acid solution before adding the $NaHCO_3$ was red owing to the presence of pervanadic acid, indicating the presence of much H_2O_2; on neutralising with $NaHCO_3$ it became yellow; and the final HNO_3 solution was also pale yellow. The solution was tested for H_2O_2 with a titanium solution; a distinct colour was obtained. These results show that much but not all of the H_2O_2 had been decomposed.

*P. 58*b*, N. 2: *Detection of Chromic Acid in the Presence of Uranium and Vanadium by* H_2O_2.—A mixture containing 1 mgrm. Cr, 100 mgrms. U, 100 mgrms. Zn, and 100 mgrms. Al as nitrates, and 100 mgrms. V as Na_3VO_4 was treated with NaOH and Na_2O_2 by P. 52; a deep red solution resulted and there was no residue. The solution was made acid with HNO_3, being cooled carefully during the process. Just enough acid was added to dissolve the precipitate that formed. To about one-fourth of the solution in a test-tube was added a little ether and about 1 cc. H_2O_2; the ether layer became blue. The water layer was red before H_2O_2 was added, showing the presence of pervanadic acid. The experiment was repeated with 2 mgrms. Cr, 100 mgrms. U, and 100 mgrms. V; the result was the same. After testing for chromium the remainder of the solution was treated by *P. 58*a*, the solution was cooled, made just acid with HNO_3, and one-tenth of it tested for chromic acid with H_2O_2; a good blue colour was obtained. The remainder of the solution was made somewhat more strongly acid and evaporated to half its volume; the test for chromic acid was then made with half the solution; no blue colour was obtained, showing that the chromic acid had been reduced on boiling.

Action of H_2O_2 *on Uranium Salts.*—To 10 mgrms. U as $UO_2(NO_3)_2$ in 20 cc. were added 1 cc. HNO_3 (1·20), 1 cc. 3 per cent H_2O_2, and a little ether; the yellow colour of the solution did not change, and the ether layer remained colourless.

*P. 58*b*, N. 4: *Precipitation of Chromate by Lead Nitrate.*—Several solutions each containing 0·5 mgrm. Cr as K_2CrO_4, 2 grms. $NaNO_3$, and 1 grm. $NaHCO_3$ in 100 cc. or 70 cc., were made distinctly acid with HNO_3, shaken to expel CO_2, and neutralised exactly with NaOH; varying amounts of HNO_3 (1·20) were added, and finally known volumes of a 20 per cent lead nitrate solution. The results are shown in the following table:—

Initial volume. Cc.	Volume of HNO_3 (1·20). Cc.	Volume of lead nitrate solution. Cc.	
100	1·5	10	Precipitate in 1 or 2 mins.
100	2·5	20	Precipitate in 3 or 4 mins.
100	5·0	30	No precipitate in 30 mins.
70	1·5	10	Precipitate in 2 or 3 mins.
70	2·5	10	Precipitate very slowly.
70	2·5	20	Precipitate in 3 to 5 mins.

The last two experiments were repeated with 6 grms. $NaNO_3$ (instead of 2 grms.); only very small precipitates were obtained in half an hour, even with 20 cc. $Pb(NO_3)_2$ solution, showing that the presence of much $NaNO_3$ prevents the precipitation of $PbCrO_4$.

Behaviour of Vanadate and Uranate towards Lead Nitrate.—Several solutions, each containing 100 mgrms. V as Na_3VO_4, 2 grms. $NaNO_3$, and 1 grm. $NaHCO_3$, in 100 cc. were acidified with HNO_3, shaken, and then neutralised exactly with NaOH; 1·5 to 3 cc. of HNO_3 (1·20) and 10 to 30 cc. of a 20 per cent lead nitrate solution were added, and the mixture allowed to stand thirty minutes; with 3 cc. HNO_3 there was no precipitate even with 30 cc. $Pb(NO_3)_2$; with 1·5 and 2 cc. HNO_3 there was none with 10 cc. $Pb(NO_3)_2$; but a small one with 20 cc., which was however very slight when 2 cc. HNO_3 were used. The experiments were repeated with an initial volume of 70 cc.; the results were nearly the same, except that the precipitate when formed were somewhat larger.

A solution containing 100 mgrms. U as $UO_2(NO_3)_2$, 2 grms. $NaNO_3$, and 1 grm. $NaHCO_3$ in 100 cc. was neutralised with HNO_3, and an excess of 1 cc. HNO_3 (1·20) was added; finally 20 cc. 20 per cent $Pb(NO_3)_2$ were added; no precipitate separated in several hours.

Precipitation of Aluminium, Beryllium, or Lead by Sodium Phosphate in *P. 58c.—0·5, 1, and 2 mgrms. Al as nitrate, in solutions containing 2 grms. $NaNO_3$, 2 grms.

* From the *Journal of the American Chemical Society*, xxx., No. 4.

NH_4NO_3, and 5 cc. 30 per cent acetic acid in a total volume of 100 cc. were heated to boiling; flocculent white precipitates separated in each case, the results showing that this is a very good method of estimating small amounts of aluminium.

The experiments were repeated with 0·5, 1, and 2 mgrms. Be as chloride; flocculent white precipitates resulted except in the experiment with 0·5 mgrm. The filtrate in the experiment with 2 mgrms. was estimated to contain about 0·5 mgrm. Be.

The experiments were repeated with 1 and 2 mgrms. Pb as nitrate; a distinct precipitate was obtained with 2 mgrms. but only a very small one with 1 mgrm. Pb.

Oxidation of Hypovanadic Acid by Bromine.—50 mgrms. V as Na_3VO_4 and 1 grm. Pb as $Pb(NO_3)_2$ were dissolved in 2·5 cc. HNO_3 (1·20) and 100 cc. water; the mixture was saturated with H_2S in the cold, filtered, and the filtrate was boiled; the cold solution had a blue colour, but on boiling sulphur separated and the colour became deeper. The sulphur was filtered off, bromine water added until the bromine odour was distinct after shaking, and the mixture was boiled; the colour was still blue. A small excess of bromine was again added; the solution was still blue. The experiment was repeated except that several drops liquid bromine were added, and the mixture shaken, and allowed to stand two or three minutes; the bromine was then boiled off; the solution was yellow. The filtrate was treated by *P. 58*c*; no precipitate separated.

Behaviour of Vanadyl Salts and Vanadates towards Sodium Phosphate.—50 mgrms. V as Na_3VO_4 and 1 grm. Pb as $Pb(NO_3)_2$ were dissolved in 2·5 cc. HNO_3 (1.20) and 100 cc. water; the mixture was saturated with H_2S, filtered, boiled, and filtered again. The blue filtrate was treated by *P. 58*c*, 2 grms. $(NH_4)_2SO_4$ and 2 grms. Na_2HPO_4 being added; on warming, a large, flocculent, bluish white precipitate separated. The experiment was repeated except that the vanadyl salt was first oxidised with liquid bromine as described in P. 58*b*; no precipitate separated in *P. 58*c*.

*P. 58*c*, N. 1: *Precipitation of Uranyl Ammonium Phosphate.*—See Kern. (*Journ. Chem. Soc.*, 1901, xxiii., 705—10).

Detection of Small Amounts of Uranium.—0·3, 0·5, and 1 mgrm. U as $UO_2(NO_3)_2$ were dissolved in separate experiments in 100 cc. water containing 5 cc. 30 per cent acetic acid and 3 grms. $NaNO_3$, and treated by P. 58*c*; white flocculent precipitates separated in each case, but that with 0·3 mgrm. was very small. The precipitates were filtered off and tested by P. 58*d*; in the experiment with 0·3 mgrm. U the ferrocyanide test failed, but was very satisfactory in the other two cases. The experiment with 0·3 mgrm. U was repeated except that 0·5, 4, and 6 grm. respectively $(NH_4)_2SO_4$ (instead of 2 grms.) were added; very small precipitates of uranyl ammonium phosphate were obtained in each case, but the ferrocyanide test failed. This shows that there is no advantage in adding more than 2 grms. $(NH_4)_2SO_4$. The experiments with 0·5 and 1 mgrm. U were repeated, except that no ammonium salt was added; with 1 mgrm. the result was satisfactory, but with 0·5 mgrm. the confirmatory failed.

The first experiments with 0·3, 0·5, and 1·0 mgrm. U were repeated in a volume of 40 cc. instead of 100 cc.; a distinct phosphate precipitate resulted in each case, and the ferrocyanide test was satisfactory, even with 0·3 mgrm. With 0·2 mgrm. a small phosphate precipitate formed, but the confirmatory test failed. The experiment was repeated with 1·0 mgrm. U, except that 0·3 grm. $Na_2HPO_4.12H_2O$ was added instead of 2 grms.; the confirmatory test failed, showing that a large excess of Na_2HPO_4 is necessary. The experiment with 0·3 mgrm. U was repeated except that 10 cc. acetic acid was used instead of 5 cc.; the confirmatory test failed, showing that a large excess of acetic acid makes the phosphate precipitation less complete.

Separation of Uranium and Vanadium by Phosphate.—100 mgrms. U as $UO_2(NO_3)_2$, 50 mgrms. V as Na_3VO_4, and 1 grm. NH_4NO_3 were dissolved in a few drops HNO_3 and 30 cc. water. The mixture was neutralised with NH_4OH; a large pale precipitate of uranyl ammonium vanadate separated. 10 cc. 30 per cent acetic acid were added; the precipitate did not dissolve. 5 cc. 10 per cent ammonium phosphate were added, the mixture was heated to boiling, allowed to stand for fifteen minutes, and filtered. The filtrate was tested for vanadium by P. 58*e*; a large quantity was found. The precipitate was washed with dilute NH_4NO_3 solution, dissolved in dilute hydrochloric acid, and the phosphate precipitation repeated; less than 1 mgrm. V was now found in the filtrate. The phosphate precipitate was treated in the same way; less than 0·2 mgrm. V was found in it. The complete experiment was repeated except that the mixture containing the uranium ammonium vanadate precipitate and the acetic acid was heated to boiling, cooled, and allowed to stand over night before the phosphate was added; the result was the same, showing that the vanadium passes into the filtrate even when it is first precipitated in combination with the uranium.

*P. 58*c*, N. 4: *Precipitation of Uranyl Hydrogen Phosphate.*—See Kern (*Journ. Am. Chem. Soc.*, 1901, xxiii., 705).

*P. 58*d*, N. 1: *Behaviour of Uranyl Salts towards Potassium Ferrocyanide.*—Known amounts of $K_4Fe(CN)_6$ solutions were added to solutions containing 0·5 mgrm. U as $UO_2(NO_3)_2$, 1 cc. HCl (1·12), and 10 cc. nearly saturated NaCl solution; with 4 cc. of a 3 per cent ferrocyanide solution a brown colour appeared only after forty minutes, with 10 cc. a brown precipitate separated in about ten minutes, while with 10 cc. of a 10 per cent ferrocyanide solution a precipitate separated in a minute or two, showing that a large excess of $K_4Fe(CN)_6$ is needed to make the test delicate. The experiment was repeated except that 0·5 cc. HCl (1·12) was added instead of 1 cc., 10 cc. 3 per cent ferrocyanide solution being added; a brown precipitate separated in a minute or two. This experiment was repeated with 0·1 and 0·05 cc. HCl (1·12); brown precipitates separated at once. The experiment was repeated without the addition of any acid; no brown colour appeared. The experiment was repeated, adding 5 cc. HCl (1·12); no brown precipitate separated in one hour, but the solution became blue and a blue precipitate separated slowly on account of the decomposition of the ferrocyanide. These experiments show that a little acid must be present, but that much acid makes the test less delicate.

0·1 and 0·2 mgrm. U as $UO_2(NO_3)_2$ were treated by *P. 58*d*, a few mgrms. PO_4 as Na_2HPO_4 being added; a good test was obtained with 0·2 mgrm., but only a very poor one after several minutes with 0·1 mgrm., showing that 0·1 mgrm. is about the limit of detectability, and that phosphate does not interfere with the detection of 0·2 mgrm. U.

The experiment with 0·5 mgrm. U and 0·5 cc. HCl (1·12) was repeated, except that water was added instead of NaCl solution; a dark red colour resulted, and no precipitate separated out in one hour, showing that NaCl is needed to coagulate the colloid.

(To be continued).

Royal Instititution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 7th inst., Sir James Crichton-Browne, M.D., F.R.S., Treasurer and Vice-President, in the Chair. Dr. W. S. Anderson Griffith was elected a Member. His Serene Highness Albert Prince of Monaco, Membre de l'Institut, was elected an Honorary Member. Dr. F. Walker Mott, F.R.S., was elected Fullerian Professor of Physiology in the Royal Institution. The Special Thanks of the Members were returned to Dr. Ludwig Mond for a donation to the Fund for the Promotion of Experimental Research at Low Temperatures.

THE MONUMENT TO ROBERT BUNSEN.

By NICHOLAS KNIGHT, Cornell College, Mount Vernon, Iowa.

Some four or five years ago an appeal was sent out to the members of the German Chemical Society asking contributions for a suitable monument to the memory of Robert Bunsen. The monument was to be erected in Heidelberg, where the great teacher and investigator had laboured so successfully for thirty-seven years, from 1852 to 1889. The admirers of Bunsen throughout the civilised world generously responded, and with some assistance from the city of Heidelberg 70,000 marks were contributed for the memorial.

The monument was unveiled on August 1 of the present year. It consists of a life-size figure in bronze of the distinguished scientist, representing him as he appeared in 1859, about the time that he and Kirchhoff invented the spectroscope. In one hand he bears a manuscript, as if about to deliver a lecture. A flight of a few steps leads from the street to the monument. On each corner of the monument plot nearest the street is a colossal figure of white granite from the Black Forest, one representing the known sciences, and the other science awaking. The monument is not far from the Heidelberg Chemical Laboratory, a part of which was constructed under Bunsen's supervision, and was afterwards added to by his illustrious successor, the late Victor Meyer. The designer of the memorial is Professor H. Volz, of Karlsruhe, and from an artistic standpoint it is a meritorious work.

The exercises connected with the unveiling were simple but interesting and impressive. Music was furnished by the city orchestra, led by Professor Grau. Professor Theodore Curtius, the director of the Heidelberg Laboratory, the successor of Bunsen and Victor Meyer, as a member of the monument committee, gave an interesting detailed history of the enterprise. Professor Bernthsen, representing the industrial chemists, spoke at length of the great debt applied chemistry owes to the investigations of him to honour the memory of whom they were assembled. He spoke of Bunsen's contributions to industrial chemistry by the spectroscope, by his discovery of important technical analytical methods, by his work in volumetric analysis, contributing to the subject a new chapter on iodometry; by his studies in gas analysis; by his improved methods of iron production, and by his separation of various metals by electrolysis. Bernthsen was formerly a student and colleague of Bunsen, and he could speak with some authority. The mayor, Dr. Wilckens, accepted the monument in the name of the university city. Representatives of the German Chemical Society and a score of similar organisations deposited upon the monument laurel wreaths and other floral tributes suitably inscribed, as a mark of esteem for the man who so ably served his day and generation. Besides the scientific organisations, many of the German universities and technical schools sent their representatives and floral offerings to do honour to the occasion, which proved a notable day in the history of the city. The exercises were largely attended, and several members of Bunsen's family were interested spectators.

Bunsen was not only one of the foremost scientists of his day, but he was a good citizen and an amiable man, beloved by all classes. He received many honours in his lifetime. The name of the street on which he lived during the ten years that he was professor *emeritus* was changed to Bunsen Strasse—rather an unusual honour, but one richly deserved.

Bunsen came to Heidelberg as professor at the age of forty-one. During the thirteen years previous he had served the Universities of Breslau and Marburg, at both of which his work justified the expectations that were realised at Heidelberg.

Some of the visitors to the unveiling ceremonies wandered to the cemetery of the old university town on the Neckar, and sought out the grave of the great scientist. The monument is plain and simple, and bears a simple inscription. The mound is covered with rhododendrons. Not far away is the granite block, almost overgrown with ivy, which marks the last resting-place of that other world renowned scientist, Victor Meyer, the worthy successor of the immortal Bunsen.

NOTICES OF BOOKS.

Hints for Crystal Drawing. By Margaret Reeks. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1908.

The difficulties with which the student of crystallography meets in crystal drawing are of considerable magnitude, and both teachers and pupils will welcome this lucid exposition of the simplest methods of dealing with the different systems. The author's solutions of the graphical problems are frequently most ingenious, and even the student whose knowledge of both mathematical drawing and crystallography is small will find that the easy stages by which he advances to the more complicated forms help him to overcome difficulties by degrees, and to acquire a thorough knowledge of each crystalline system. Clinographic projections are employed, and the clear illustrations of the most complex as well as the simpler forms make the text very easy to follow. Every student of mineralogy should have some knowledge of the elements of crystal drawing, and he will be able to find no better book from which to learn it; as a supplement to larger works on crystallography the book must be regarded as one of great value.

Einführung in die Kolloidchemie. ("Introduction to the Chemistry of Colloids"). By Dr. Viktor Pöschl. Dresden: Theodor Steinkopff. 1908.

This pamphlet gives a brief abstract of the most important developments of our knowledge of colloid chemistry, since the first colloidal substances were prepared by Graham, who, in 1861, laid the foundations of the subject. The nomenclature which has now been generally adopted is explained, and the peculiar properties of colloids are discussed as well as the preparation of the different groups of compounds. An interesting review is given of ultra-microscopic methods of research, and the fundamental principles of modern theories are very shortly expounded. The importance of a knowledge, even if only meagre, of the chemistry of colloidal substances is rapidly increasing, and its special relations to other sciences and to chemical industries are continually being extended. Every student of chemistry and every technical chemist should make time to study carefully some such work as this, which in the smallest possible space gives an adequate account of an interesting subject.

Synthetische und Isolierte Riechstoffe und deren Darstellung. ("Synthetic and Isolated Perfumes and their Preparation"). By Dr. Rudolf Knoll. Halle-a.-S.: Wilhelm Knapp. 1908.

The first and general part of this monograph gives accounts of the properties of perfumes, and discusses shortly the connection between chemical constitution and odour. This highly interesting subject, upon which important work has been done, is perhaps regarded as of a too purely scientific nature to come much within the scope of a book which is meant to be of special service to practical chemists, or to those who are just beginning their technical career. The account of general methods of synthesising perfumes includes descriptions of the preparation on a large scale of some substances, such as phosphorus trichloride, which are employed in making perfumes. The special part of the book deals with the constitution, properties, and preparation of compounds of aromatic odour, those belonging to the aldehyde and ketone classes being

grouped together. The methods of preparing them and the apparatus usually employed are described in outline, and in spite of the difficulty in getting information about processes which very often the manufacturers wish to keep to themselves as much as possible, the most representative methods on a technical scale are well described, as well as the purely laboratory processes of which they are modifications.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvii., No. 18, November 2, 1908.

Separation of Tungstic Acid and Silica.—Paul Nicolardot.—Silica is not attacked even when combined with tungstic acid when it is treated with a mixture of imperfectly dried air and carbon tetrachloride vapour. Chloroform at 500° attacks tungstic acid, but has no action on silica; the vapours may be cooled in a condenser, and the method can be used to obtain tungstic acid free from silica.

Determination of the Atomic Weight of the Simple Ponderable Substance, Pantogen.—G. D. Hinrichs.—Hydrogen is the simplest of all the chemical elements, the least condensed form of ponderable material, and by the study of it the author has endeavoured to arrive at the atomic weight π of the fundamental substance pantogen. The atomic weight of hydrogen (O = 16) is very approximately $H = 16/16 - \frac{1}{\pi} = 1{\cdot}00787$. From theoretical considerations the author deduces that the excess over H = 1 of the true value of the atomic weight of hydrogen is the exact value of the atomic weight of pantogen for O = 16 or C = 12. The union of pantogen atoms in cubes, prisms, &c., gives the atoms of other elements such as nitrogen, oxygen, fluorine, and from the number of pantogen atoms forming the atom of the element its atomic weight may be calculated.

Zinc Phosphides.—Pierre Jolibois.—By pouring fused zinc on to red phosphorus and heating in a Perrot furnace crystals of a definite compound are obtained. Its formula is Zn_3P_2. With concentrated or dilute hydrochloric acid it yields PH_3 quantitatively according to the equation $Zn_3P_2 + 6HCl = 3ZnCl_2 + 2PH_3$. When phosphorus vapour acts on this compound *in vacuo* at 400° a brown mass is obtained, from which a black compound can be isolated. Its formula is ZnP_2. It dissociates at 500° into P_2Zn_3 and phosphorus. With hydrochloric acid it yields PH_3 and the solid hydride P_2H.

Influence of Neutral Salts on the Hydrolysis of Iron Perchloride.—G. Malfitano and L. Michel.—The hydrolysis of $FeCl_3$ in presence of KCl is either accelerated or retarded according to the relative proportions of the two salts. The composition and state of division of the colloidal matter are both affected, though the potassium chloride does not enter into the composition of the colloid. The other chlorides, NaCl, NH_4Cl, $BaCl_2$, $MgCl_2$, behave similarly, variations in their effect being due to their different coefficients of electrolytic dissociation. KNO_3 behaves like the chlorides. On the other hand, K_2SO_4 and K_2HPO_4, in which the negative radicle is polyvalent, act quite differently. They always hinder hydrolysis, and the lower the temperature the less they hinder it. In presence of increasing amounts of salts the number of iron ions is diminished, and the formation of $Fe(OH)_3$ is retarded if the proportion of salt added is not sufficient to diminish ionisation, and thus the antagonistic activity of the other product of hydrolysis, the acid.

Aloësol.—E. Léger.—When potassium chlorate is added to a solution of Cape or Uganda aloes in concentrated hydrochloric acid, a mixture of chlorinated aloïns is obtained, and a substance $C_{11}H_4Cl_4O_3$, which may be made to crystallise in almost colourless needles. One of the oxygen atoms of this compound belongs to a phenol OH, and the compound may be regarded as the tetrachlorinated derivative of an unknown phenol, to which the author has given the name aloësol. Tetrachloraloësol may be separated from the substances which accompany it by treating with hot alcohol, in which it is almost insoluble. The pink raw product may be purified by crystallising in boiling acetic acid after treating the solution with animal charcoal. Nitric acid converts it into oxalic acid and perchlorinated quinone, which shows that it contains a benzene nucleus in which two chlorine atoms and a hydroxyl group are substituted, and to which the residue $C_5H_2Cl_2O_2$ is attached. This residue contains neither alcohol, acid anhydride, ether-oxide, nor quinone functions.

MISCELLANEOUS.

Royal Institution.—The following are the Lecture Arrangements at the Royal Institution, before Easter:—Prof. W. Stirling, a Christmas Course of six experimentally illustrated lectures on "The Wheel of Life," adapted to a juvenile auditory; Prof. Karl Pearson, two lectures on "Albinism in Man"; Prof. A. A. Macdonnell, three lectures on "The Architectural and Sculptural Antiquities of India"; Dr. F. Walker Mott, six lectures on the "Evolution of the Brain as an Organ of Mind"; Prof. J. O. Arnold, two lectures on "Mysteries of Metals"; Mr. William Archer, two lectures on "The Revival of Modern Drama"; Dr. Hans Gadow, three lectures on "Problems of Geographical Distribution in Mexico"; Mr. A. D. Hall, two lectures on "Recent Advances in Agricultural Science"; Prof. G. H. Bryan, two lectures on "Aërial Flight in Theory and Practice"; Prof. Sir Hubert von Herkomer, two lectures on—(1) "The Critical Faculty," (2) "Sight and Seeing"; Sir Alexander Mackenzie, three lectures on—(1) "Mendelssohn" (with Musical Illustrations), (2, 3) "Chamber Music" (with the kind assistance of the members of the Hans Wessely Quartette); and Prof. Sir J. J. Thomson, six lectures on "Properties of Matter." The Friday Evening Meetings will commence on January 22, when Dr. Alfred Russel Wallace will deliver a Discourse on "The World of Life, as Visualised and Interpreted by Darwinism." Succeeding Discourses will probably be given by Lieut.-Colonel Sir Frederic Nathan, Prof. J. G. Frazer, Prof. H. A. Wilson, Sir Henry Cunynghame, The Right Hon. the Earl of Berkeley, The Right Hon. Viscount Esher, Mr. S. G. Brown, Mr. R. Threlfall, Mr. A. S. Eddington, Prof. Sir J. J. Thomson, and other gentlemen.

MEETINGS FOR THE WEEK.

MONDAY, 14th.—Royal Society of Arts, 8. (Cantor Lecture). "Twenty Years Progress in Explosives," by O. Guttmann.

TUESDAY, 15th.—Faraday Society, 8. "Re-determination of the Electrolytic Potentials of Silver and Thallium," by F. J. Brislee. "Heats of Combustion of Aluminium, Calcium, and Magnesium," by F. E. Weston and H. R. Ellis. "Formation of Graphite by the Interaction of Magnesium Powder and Carbonates," by H. R. Ellis. "Colloidal Barium Sulphate," by E. Feilmann.

WEDNESDAY, 16th.—Royal Society of Arts, 8. "London Milk Supply from a Farmer's Point of View," by Primrose McConnell.

—— Microscopical, 8. "Workshop Microscope for the Examination of Opaque Objects" and "A Simple Method of Illuminating Opaque Objects," by J. E. Stead. "Mounting Rotifers and Protista in Canada Balsam," by Rev. E. Tozer.

THURSDAY, 17th.—Chemical, 8.30. "Silicon Researches—XI., Silicotetrapyrrol; XII., Action of Silicon Chloroform on Potassium Pyrrol; XIII., Silicon Halides and Pyridine, Acetonitrile, &c.," by J. E. Reynolds. "Affinity Values of Tropine and its Derivatives," by V. H. Veley.

THE CHEMICAL NEWS.

Vol. XCVIII., No. 2560.

ON SCANDIUM.*

By Sir WILLIAM CROOKES, D.Sc., F.R.S.

(Continued from p. 285).

Scandium Acetate, $(CH_3COO)_2ScOH,2H_2O$.

Scandium oxide after ignition does not dissolve in acetic acid. The hydroxide, however, dissolves easily, and the acetate soon separates from the liquid in the form of fine white crystals, difficultly soluble in water. The aqueous solution, evaporated over the water-bath, deposits hard crystalline crusts.

When freshly prepared, the acetate dried in the air has the composition given below. Water, however, is slowly given off, and after standing some days the salt passes into a monohydrate analogous to the formate.

When ignited, the acetate leaves a grey residue of scandia containing carbon. By ignition alone it is difficult to get it of a constant weight. The best way to analyse the salt is to moisten the weighed acetate with a few drops of nitric acid and cautiously to evaporate to dryness, heat, and ignite. In this way is obtained pure white scandia.

Analysis.

1. 7·795 grs. of acetate left 2·449 grs. of scandia, = 1·5859 grs. of scandium.
2. 7·133 grs. left 2·270 grs. of scandia, = 1·4697 grs. of scandium.
3. 19·035 grs. left on ignition 6·000 grs. of scandia, = 3·8848 grs. of scandium.

	Theory.		Experiment.		
			1.	2.	3.
Sc	44·100	20·49	20·35	20·60	20·41
$(CH_3COO)_2$ OH .. .. $2H_2O$ . ..	171·088	79·51	79·65	79·40	79·59
	215·188	100·00	100·00	100·00	100·00

After being exposed to dry air for several days, the dihydrate loses one molecule of water of crystallisation, and becomes a monohydrate—

$(CH_3COO)_2ScOH,H_2O$.

Analysis.

14·690 grs. left 5·262 grs. of scandia, = 3·4075 grs. of scandium.

	Theory.		Experiment.
Sc	44·100	22·37	23·19
$(CH_3COO)_2$ .. OH . .. .. H_2O	153·072	77·63	76·81
	197 172	100·00	100·00

Scandium Propionate, $(C_2H_5COO)_2ScOH$.

Propionic acid readily attacks scandium hydroxide, forming a difficultly soluble white amorphous salt. On evaporating the excess of acid the scandium propionate is left as a voluminous white powder. 100 parts of cold water dissolve 1·23 parts of scandium propionate, the greater part being precipitated on heating the solution, and re-dissolved on cooling. When boiled in water, the salt floats greasily about the surface. The propionate is easily soluble in alcohol even in the cold, and when the alcoholic solution is allowed to evaporate the propionate is deposited as a mass of minute spherical concretions with no appearance under the microscope of crystalline structure.

The scandium propionate so obtained has the formula—

$(C_2H_5COO)_2ScOH$.

Analysis.

15·978 grs. on ignition yielded 5·287 grs. of scandia, = 3·424 grs. of scandium.

	Theory.		Experiment.
Sc	44·100	21·29	21·43
OH .. .. .. $(C_2H_5COO)_2$ ..	163·088	78·71	78·57
	207·188•	100·00	100·00

Scandium Butyrate, $(CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}COO)_2ScOH$.

When scandium hydroxide is heated with butyric acid, a white amorphous and difficultly soluble salt is produced. When boiled in water, the butyrate softens to a plastic mass, becoming hard and brittle on cooling. Like other scandium salts of the fatty acids, scandium butyrate is more soluble in cold than in hot water, and is precipitated from a cold solution on boiling. It is easily soluble in alcohol. The solution in cold water, evaporated over a water-bath, leaves a residue which under the microscope is seen to consist of minute spherical groups, radiating from a central nucleus.

Analysis.

6·251 grs. of butyrate yielded on ignition 1·826 grs. scandia, = 1·182 grs. of scandium.

	Theory.		Experiment.
Sc	44·100	18·75	18·91
OH .. .. .. $2(C_3H_7COO)$ ..	191·120	81·25	81·09
	235·220	100·00	100·00

Scandium Iso-butyrate, $\left(\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH{\cdot}COO\right)_2ScOH,2H_2O$.

This salt is prepared in a similar manner to the butyrate, which it much resembles in appearance. It is more soluble in cold than in hot water, a saturated cold solution becoming thick and depositing amorphous flakes when heated. On cooling the liquid becomes clear again; in this respect it closely resembles calcium butyrate. It is very soluble in alcohol and is precipitated by water from the alcoholic solution.

The formula of the iso-butyrate differs from that of the butyrate in having two molecules of water of crystallisation :—

$(C_3H_7COO)_2ScOH,2H_2O$.

Analysis.

9·994 grs. of scandium iso-butyrate gave on ignition 2·550 grs. of scandia, = 1·651 grs. of scandium.

	Theory.		Experiment.
Sc_2.	44·100	16·26	16·52
OH .. .. .. $2(C_3H_7COO)$ .. $2H_2O$	227·152	83·74	83·48
	271·252	100·00	100·00

* A Paper read before the Royal Society, April 30, 1908.

SCANDIUM ISO-VALERATE,

$(C_4H_9COO)_2ScOH,2H_2O.$

Scandium hydroxide is readily attacked by aqueous iso-valeric acid, forming a white amorphous salt, soluble in cold water, precipitated on boiling, and again dissolved on cooling. Dried over sulphuric acid the iso-valerate has the composition—

$(C_4H_9COO)_2Sc(OH),2H_2O.$

Analysis.

10·902 grs. of scandium iso-valerate left on ignition 2·493 grs. of scandia, = 1·614 grs. of scandium.

	Theory.		Experiment.
Sc	44·100	14·74	14·80
OH .. .. .. }			
$2(C_4H_9COO)$ .. }	253·184	85·26	85·20
$2H_2O$ .. .. .. }			
	299·284	100·00	100·00

SCANDIUM OXALATE,

$Sc_2(C_2O_4)_3,5H_2O.$

Scandium oxalate comes down as a white crystalline powder when oxalic acid or ammonium oxalate is added to a solution of scandium. If much free mineral acid is present the precipitation is not immediate; it begins by a cloudiness, which in a few minutes increases to a crystalline precipitate, a little scandium oxalate remaining in the solution. It is slightly soluble in water, weak acids, and more so in solution of ammonium oxalate. On boiling a mixed oxalate from wiikite in a solution of ammonium oxalate the portion dissolved was richer in scandium than the insoluble part. Attempts were made to effect a separation of scandia from the accompanying earths by making use of this fact. A mixed oxalate of crude earths was boiled in a strong solution of ammonium oxalate and then filtered, and this operation was repeated on the residue several times. Ultimately the most soluble and the least soluble earths were separated and their spectra photographed. The most soluble earth was nearly all scandia, with a little yttria, and traces of ytterbia, titania, and lime. The least soluble contained more yttria than scandia, but not much of either. By a repetition of this process it would not be difficult to effect a good separation of scandia and yttria; I think the fused nitrate process is simpler and quicker.

When crude scandium oxalate is boiled in a solution of ammonium oxalate a partial separation of the earths is effected, but it is less complete than when ammonium carbonate is used as a solvent. This is a very good method for separating scandia from zirconia, as hardly a trace of the zirconia is to be seen in the portion insoluble in hot ammonium oxalate.

According to Nilson (*Comptes Rendus*, vol. xci., p. 121), the precipitated oxalate is slightly soluble in weak acids, and even in water. I have verified this observation; care must be taken not to over-wash the oxalate, or loss will ensue, and the filtrates should be kept and worked again for scandium.

The precipitated oxalate, dried in the air, contains 5 molecules of water.

Analysis.

1. 22·445 grs., ignited at a yellow heat, left 6·988 grs. of scandia.
2. 21·873 grs. ignited left 6·806 grs. of scandia.

	Theory.		Experiment.	
			1.	2.
Sc_2O_3 ..	136·20	30·79	31·13	31·12
$3C_2O_3$ .. }	306·08	69·21	68·87	68·88
$5H_2O$ .. }				
	442·28	100·00	100·00	100·00

When the 5-hydrated oxalate is allowed to dry at the ordinary temperature over sulphuric acid, it loses 2 molecules of water and becomes a 3-hydrate—

$Sc_2(C_2O_4)_3,3H_2O.$

Analysis.

7·639 grs. left on ignition at a yellow heat 2·529 grs. of scandia.

	Theory.		Experiment.
Sc_2O_3	136·200	35·33	33·11
$3C_2O_3$ .. .. }	270·048	66·47	66·89
$3H_2O$ .. .. }			
	406·248	100·00	100·00

The 5-hydrate of scandium oxalate, dried in a hot-air oven at 100°, loses three molecules of water, and becomes a 2-hydrate—

$Sc_2(C_2O_4)_3,2H_2O.$

Analysis.

22·445 grs. lost 2·014 grs. of water.

	Theory.		Experiment.
Sc_2O_3 .. .. }	352·200	90·72	91·03
$3C_2O_3$ .. .. }			
$2H_2O$	36·032	9·28	8·97
	388·232	100·00	100·00

The hydrated oxalate, dried *in vacuo* at 100° or in air at 140°, loses all but one molecule of water and becomes a mono-hydrate—

$Sc_2(C_2O_4)_3,H_2O.$

Analysis.

1. 32·118 grs. left on ignition 11·756 grs. of scandia.
2. 15·694 grs. left 5·815 grs. of scandia.
3. 8·304 grs. left 3·010 grs of scandia.

	Theory.		Experiment.		
			1.	2.	3.
Sc_2O_3 ..	136·200	36·79	36·60	37·05	36·25
$3C_2O_3$ .. }	234·016	63·21	63·40	62·95	63·75
H_2O .. .. }					
	370·216	100·00	100·00	100·00	100·00

SCANDIUM SUCCINATE,

$$\begin{matrix} CH_2COOSc(OH)_2 \\ | \\ CH_2COOSc(OH)_2 \end{matrix} \quad H_2O = C_4H_8O_8Sc_2,H_2O.$$

This salt comes down as an insoluble white precipitate when dilute solutions of ammonium succinate and scandium nitrate are mixed. It also may be prepared by boiling scandium hydroxide in solution of succinic acid. It is slightly soluble in excess of either reagent, and is insoluble in water or alcohol. When dried in the air it forms a hard porcelain-like mass.

Analysis.

12·713 grs. of scandium succinate heated for ten hours to 180° lost 0·822 gr. of water, and when ignited to full redness it left 6·089 grs. of scandia, = 3·9431 grs. of scandium.

	Theory.			Experiment.
Sc_2 . ..	88·200		30·38	31·02
C_4	48·000			
H_8	8·064	184·064	63·41	62·51
O_8	128·000			
H_2O. ..	18·016		6·21	6·47
	290·280		100·00	100·00

Scandium Picrate,
$\{C_6H_2(NO_2)_3O\}_2ScOH,14H_2O$.

The hydroxide dissolves readily in warm solution of picric acid and separates in groups of long needle-shaped crystals of a rich yellow colour. When rapidly crystallised from a strong solution, the crystals form confused feathery masses, which on pouring off the mother-liquor turn to a felt-like mass difficult to drain. 100 parts of water at 20° dissolve 0·95 part of scandium picrate. At 9° the same quantity of water dissolves 0·37 part. Dried by exposure to cold dry air the crystals have the composition shown above.

The picrate cannot be detonated when wrapped in tin-foil and struck on an anvil with a heavy hammer. Heated in a dry test-tube it darkens, gives a slight sublimate, fuses, and at a little higher temperature faintly explodes, leaving a black flocculent residue, which burns off to pure white scandia at a red heat.

The explosion, although not violent, is sufficient to blow some of the products out of the crucible. The scandia therefore was estimated by precipitating the hot solution with ammonia in considerable excess and well boiling the liquid before filtering. Unless this precaution is taken some of the picrate precipitates as such, and slight explosions occur when the precipitate is burnt.

Analysis.

1. 27·497 grs. of picrate, dried at 100°, gave off 5·906 grs. of water.
2. 27·497 grs. yielded 2·422 grs. of scandia, = 1·569 grs. of scandium.

	Theory.		Experiment.
			1 and 2.
Sc	44·100	5·73	5·71
OH			
$2\{C_6H_2(NO_2)_3O\}$	563·180	73·20	72·81
$5H_2O$			
$9H_2O$	162·144	21·07	21·48
	769·424	100·00	100·00

When the 14-hydrate is heated to 100°, nine molecules of water go off, leaving a 5-hydrate.

$\{C_6H_2(NO_2)_3O\}_2,ScOH,5H_2O$.

Analysis.

21·657 grs. of the picrate, dried at 100°, gave 2·422 grs. of scandia, = 1·569 grs. of scandium.

	Theory.		Experiment.
Sc	44·100	7·26	7·24
OH			
$2\{C_6H_2(NO_2)_3O\}$	563·180	92·74	92·76
$5H_2O$			
	607·280	100·00	100·00

Scandium Benzoate,
$(C_6H_5CCO)_3Sc$.

Scandium benzoate comes down as a white curdy precipitate on adding a solution of ammonium benzoate to scandium nitrate solution. On boiling the solution the precipitate collects as a crystalline powder. It is slightly soluble in water and alcohol, and easily soluble in dilute mineral acids.

Analysis.

12·303 grs. of scandium benzoate left on ignition 2·204 grs. of scandia, = 1·4272 grs. of scandium.

	Theory.			Experiment.
Sc	44·10		10·83	11·60
C_{21}.. ..	252·00			
H_{15} . ..	15·12	363·12	89·17	88·40
O_6	96·00			
	407·22		100·00	100·00

(To be continued).

THE DECOMPOSITION OF YTTERBIUM INTO ITS ELEMENTS.*

By C. AUER von WELSBACH.

(Concluded from p. 225).

The Spark Spectra.

To produce the luminous vapour I used exclusively my new spark apparatus which depends upon the application of the spark at break, and which when it is properly managed and a rotating platinum pole is used, easily allows the spectra of most elements to be obtained almost pure and free from the lines of the pole substance as well as from those of air.

As regards their character, the spectra with the spark at break are in many respects intermediate between the arc spectra and the peculiar spark spectra. They are sometimes more like the former and sometimes resemble the latter, and at any rate with the arrangement I used, this variation in character does not seem to occur according to any fixed rule.

Thus, for example, the spark spectrum of platinum is almost identical with the arc spectrum, while the spectra with the spark at break of the rare earths agree perfectly with the spark spectrum, as Exner and Haschek's measurements show.

The lines of the arc spectrum of platinum coincide exactly with the lines of the spark at break spectrum. In no case could the slightest difference be detected.

The spark spectra of the two new elements are relatively poor in lines, but they belong to the brightest known. This holds good especially for cassiopeïum. The few lines which this substance has in the optical part of the spectrum somewhat recall the magnificent barium spectrum. Besides these lines the Cp spectrum is characterised by two channelled bright shining bands in the green and blue, somewhat recalling the Cy-spectrum. While the band in the green consists of several fine lines that in the blue is of a nebulous character. With the dispersion which my apparatus possesses the resolution into lines could not be effected. The light maxima lie towards the refrangible part of the spectrum; thus the structure is the opposite of that of the Cy bands.

The spectrum of Ad is much richer in lines than that of Cp, both in the optical and ultra-violet parts. Most of the Yb lines occur in it. To produce the spectrum a Rowland's concave grating of the old kind was used for all the photographs taken for reproduction or measurement. It possesses 14,473 lines per English inch, and a radius of curvature of about 2 m. The length of the divided surface amounts to about 54 mm. I prefer this grating, with which I have taken all comparison photographs of late years, to others, because, besides excellent definition, it possesses the property so valuable for my spectral work of not distributing the diffracted light uniformly, but concentrating it in certain spectral regions which are well situated for taking the photographs (*cf.*, H. Kayser, "Handbuch der Spektroskopie," vol. i., p. 433). For this reason I often succeeded in taking spectrographs of brilliant sharpness for the whole length of the spectrum, using only a few milligrammes of the substance under investigation.

If a sunbeam is allowed to fall on this grating in the direction of the optical axis, and the diffracted light is reflected towards a wall, the spectrum of the first order appears bright on one side, while that on the other side is quite faint, and the same holds good for the spectra of the next higher orders. Curiously enough the spectrum of the first order breaks off suddenly at about $\lambda 3300$, but occurs again in the second order of the same side with such great intensity that the photographs for the first and second order could be taken simultaneously with almost the same effect. In consequence for the spectral region from 3300 towards the shorter wave-lengths I have always taken photographs in the second order.

* *Monatshefte für Chemie*, February, 1908.

The result of the great sensitiveness of our ordinary dry plates towards light of a short wave-length is that the zone within which lines of the first and second order can be taken together is fairly large, comprising about 800 A.U.

Since in many experiments, as for instance in testing very expensive substances, it is of great importance to obtain a spectral region comprising several thousand A.U. in one single photograph suitable for measuring or comparison, I used a concave mirror silvered on the inner surface to collect the light instead of the usual quartz lens.

All waves of 235 $\mu\mu$ and upwards were not reflected to an appreciable extent by the mirror, as silver is transparent to such rays, so that λ4600 of the first order could be obtained free from lines of the second order. The part of the spectrum suitable for measurement taken in one photograph on ordinary bromine plates reaches from λ4600 to 2500. The use of concave mirrors is to be recommended on account of the great strength of the light which the spectra receive, especially if the parts of the visible spectrum which do not act on the ordinary plates are to be taken. Moreover, this is of great importance for many comparative chemical investigations apart from wave-length measurements. For it is in this part of the spectrum that differences in the intensity of the lines of two spectra produced by alterations in the mixture are to be detected long before they can be recognised in the ultra-violet part.

Grating, slit, as well as the boxes for the cassettes made of flexible material, are placed at fixed positions on a strong frame made of perfectly dry mahogany. The whole apparatus is enclosed in a roomy box made of mahogany and covered on the interior with dull black velvet. The frame, lying freely on rubber balls, rests on an iron stand. The whole apparatus can be moved in any direction, and it is not more difficult to transport than another larger spectral apparatus. I give a fuller description of the whole arrangement, which presents many novelties, in my book, "Spektroskopische Methoden der Analytischen Chemie," which will shortly be published.

Almost all photographs were taken on very sensitive dry plates of the finest grain, which were about 0·8 mm. thick and thus flexible. As such thin glass plates can be cut very sharply after a little practice with a suitable diamond, without splitting the edge, it is easy to place two or more spectra taken on the plates very near to one another, so that they can conveniently be compared directly with one another, provided that they were photographed under exactly the same conditions.

Owing to the fixed position of grating, slit, and plate only a certain region of the spectrum was normal.

I did not ascribe any great importance to this because I did not originally intend to measure whole spectra by determining accurate wave-lengths, but I was rather aiming at getting the spectra in forms in which they could be directly compared with one another. For all those cases in which lines have to be measured, or in which it is a question of determining accurately the position of a line, I wished to obtain the desired information within a few minutes without great trouble and without elaborate apparatus. For this reason I abandoned the usual classical comparison methods and measured the spectra by photographed scales corresponding almost exactly to the length of the spectrogram. But the lack of sharpness of the divisions on the printed scales of course diminished the accuracy of the measurements, very often more than was expected, and also strained the eye very considerably.

I succeeded later in avoiding this error, and photographed the scale so sharply that it allowed of a considerable enlargement without specially straining the eyes. This method was suited for taking fairly accurate measurements; thus in the spectrum of the second order the A.U. corresponded to about 0·27 mm. of the photograph. I used the platinum lines as standard lines. I took the wave-lengths of these from H. Kayser's tables of the arc spectrum of platinum. I rounded off the numbers, which give the wave-lengths to thousandths of an A.U., to two places of decimals for my purpose.

The differences which exist between the wave-lengths of Kayser (arc spectrum) and those of Exner and Haschek (spark spectrum) mostly account for the discrepancies which appear between my measurements and those of the latter investigators.

As the number of platinum lines in the optical part is too small to make it possible to take the necessary measurements I used the lines of the platinum spectrum of the second order, which I took between the two other spectra, much shortened and thus made easily recognisable. The platinum lines of the first order contained in the spectrum of the substance to be tested thus provided a control of any displacement.

I could not prove any deflection of the lines in consequence of the high altitude of the place at which the photographs were taken (800 m. above the sea level).

The breadth of the slit was always about 0·01 mm.

As source of current a storage battery of terminal voltage 50 volts, built for lighting supply, was used. In all the photographs described in this article a constant resistance of 25 ohms was placed in the circuit. The intensity available to produce the spark was therefore fairly small, so that the positive poles made of platinum wire 1·4 mm. thick only glowed faintly at their ends.

I used ethyl red as sensitiser for the photographs in the visible part. As various accounts have been published of the sensitising action of this dye I may regard it as well known. On account of their high sensitiveness I have mostly worked with wet plates, and I always exposed them immediately after sensitising, because if they lie by, on account of the carbon dioxide contained in the air, the sensitiveness rapidly decreases. I brushed off adhering drops of water by means of a broad fine brush. It is scarcely necessary to point out that the gradation of the sensitised plates leaves much to be desired.

Partly that I might better estimate the intensity of the lines, and partly in order to recognise for certain any impurities present, I took several photographs with different times of exposure under as far as possible the same conditions and for the same region of the spectrum. Thus for the region from λ4600 to 2500 I used exposures of 1, 10, 100, 180, and 200 seconds, and with Cp 500 seconds so as to find any trace of impurity present. In the visible part I was satisfied with three photographs with exposures of 60, 200, and 600 seconds. The estimation of the intensity of the lines in this part I also performed occasionally by ocular observation, because the sensitised plates possess limits of sensibility quite different from those of ordinary plates and much more irregular. Naturally these, like other numbers, are devoid of scientific foundation.

In a table in the original paper I have collected the results of the measurements obtained with the help of the above named plates, in so far as they refer to the more intense lines.

In the region 4600 to 2500 all strong lines are marked which were to be seen on the plates after an illumination of 100 seconds, excluding those which came from the substance of the poles, such as platinum lines and some lines of Pd, Ir, and Cu.

I have chosen this particular time of illumination because these photographs were very much like those of Exner and Haschek, as far as the intensity of the lines is concerned, and thus the statements of these investigators could be compared with mine. For completeness sake I have also taken those wave-lengths which Exner and Haschek give for the arc spectrum of ytterbium. The spectral work of Exner and Haschek, which is of such importance in chemical investigation, I assume to be known.

From the relative intensity of the lines for the region 4600 to 2500 it is seen that the spectrum with the spark at break of the rare earths in question is very similar to the spark spectrum produced by high tensioned currents.

For all measurements made in the region of the first order, *i.e.*, from 4600 to 3300, I have given Exner's numbers generally unaltered when those obtained by me did not differ from them by more than 0·05 A.U. For the measure

ments in the reign of the second order I have lowered the difference to about 0·03 A.U. In this region there are consequently many numbers which differ from those of Exner. These differences, however, in most cases are to be ascribed to the differences already mentioned as existing between Kayser's and Exner's numbers.

To supplement the table I have added a photographic representation of the spectra. Although the difficulties of getting a good reproduction of a spectral photograph are very great, they do not nevertheless seem to me to be worth taking into account in comparison with the advantages which a true picture offers. For, firstly, the spark spectra of the new elements in relation to one another and also to ytterbium—and this is much the most important in this work—can be described shortly and intelligibly only by the help of good pictures; secondly, we are dealing with rare elements difficult to prepare, which even in the small quantities necessary to obtain a spark are either obtained only with great difficulty or not at all, although their spectra, and this holds good especially for Cp, are characterised not only by the position of the lines but also by their constitution and character.

With good reproductions with the help of wave-length tables we can easily take photographs directly comparable for each instrument, photographs by means of which a spectrum to be investigated can be quickly and easily tested. This is all that is of importance in many cases of chemical investigations. It is of course supposed that to produce the luminous vapour giving the spectrum the same arrangements are made under the same experimental conditions. All pictures were obtained directly by the photographic method. They include the region from 6000 to 2600.

To develope the plates I used only hydroquinone. In order to get the half tones as well as the fainter lines, according to the advice of practical photographers I avoided everything which could appreciably increase the contrasts. The pictures have thus undoubtedly lost much as engravings, but have gained considerably in clearness.

To produce the spark I used only pure aqueous nitrate solutions containing about 10 per cent of oxide.

The general examination of the figures shows the great difference between the spectra of Ad and Cp in the optical part, the region photographed on the sensitised plates. Here the spectrum of ytterbium, except of course in so far as the intensity of the lines is concerned, plainly divides itself into the two others. This is not quite the case in the violet and ultra-violet part, the special region of our highly sensitive bromine plates. Although the ytterbium spectrum in these regions also appears fairly clearly as the sum of the two other spectra, these latter are much more like one another. For almost every strong line in the spectrum of one element has a corresponding line visible, if faint, in the spectrum of the other. I have previously alluded to this peculiar phenomenon, which is important in the application of spectral analysis in analytical chemistry.

In the given case the objection might be raised that because the time of illumination was the same for all plates, the violet and ultra-violet rays, in consequence of the high sensitiveness to light of the plates, would act more strongly than those situated in the visible part. This may hold good for the yellow rays, but it is not true for the blue-green. The true causes are much more obscure.

The differences mentioned appear still more clearly when the platinum lines are considered. As only platinum poles were used to produce the spark, all substances brought on to the poles during the production of the spark must to a certain extent be adulterated with platinum, or rather the substance giving the spark consists of an alloy of earth metal and platinum such as can actually be shown to exist chemically in the peripheral part of the pole. Suppose the behaviour of the line λ 5301·18 in the blue-green is compared with that of the line λ 2998·09 in the ultra-violet. While the one, in spite of its extraordinary intensity, can hardly be detected in the spectrum of the earth, the other, although much less strong, is sharp and clearly visible in all spectra. In order to make this marked difference still plainer I magnified the spectral zone from 4700 to 4530 to twice its size after taking it on the sensitised plate, and also after taking it on the ordinary bromide plate. As regards the latter I must mention that it was done intentionally without a ray filter because in it some faint, but not disturbing, lines of the second order are found. The platinum line 4552·59 is observed in both parts.

In the platinum spectrum of the sensitised plate this line is very intense, but, on the other hand, it is scarcely visible in the earth spectrum; while in the platinum spectrum on the bromide plate it is not strong, it appears bright and sharp in the earth spectrum.

If now the photographs of the sensitised plates are compared ocularly with the spectrum itself a striking agreement is observed on the whole, a phenomenon which allows of a very simple explanation. What holds good for the lines described also holds good for all other lines concerned, and, as far as I can see at present, for all other spectra. The sensitiveness of the spectral reaction in the violet and ultra-violet part of the spectrum (the active region of the ordinary dry plate) is far greater than in the visible part and steadily increases in this part towards the less refrangible end. Hence in all cases in which incipient variations in mixtures are to be established the spectral tests must be performed in the visible part, and either ocularly or with wet plates as highly sensitised as possible. I have alluded to these relations very shortly here, partly because they seem to me to be important for the right estimation of the tables, and partly because I believe that the sooner they are taken into consideration the better after the previous neglect of them in chemical work.

An exhaustive treatment of them I must leave for a later article, all the more because this would not be possible without a thorough discussion of the nature of the photo-chemical processes which occur in the plate, and which still need much explanation.

In all spectra several Ca lines occur, especially λ3968·16 and 3933·80. The intensity of the first line in the wave-length tables of Exner and Haschek was denoted by 500, and that of the latter by 1000. Small traces of calcium could be detected in all preparations. It was not possible to remove it completely from the earths by the usual methods of analytical chemistry. Other methods which would have led to complete separation could not be applied owing to the small quantity of the specimens obtainable.

The constant appearance of calcium in these fractions, which it will be remembered had been obtained by fractional crystallisation from ammoniacal ammonium oxalate solutions, was very surprising. I therefore tested for calcium in these preparations. By careful precipitation of the well boiled earth metal solutions containing excess of ammonium salt with ammonia free from CO_2 I succeeded in getting a minute amount of pure calcium. The spark spectrum given by this specimen was identical with the normal spectrum of calcium; no single line showed any difference in intensity.

In the ultra-violet part of the Ad spectrum lines are to be seen which are either missing or nearly so in the ytterbium spectrum. They are the lines of elementary thulium.

Finally, I must mention that in the Cp spectrum, when the time of exposure amounted to 500 seconds, very faint iron lines and a very faint Mg line could be detected. There were no lines of other substances.

Several lines, especially in the ultra-violet, occur in all three spectra with the same intensity. I have marked them *g. l.* in the table, *i.e.*, common lines.

It is not probable that these are only apparent coincidences. For this peculiar phenomenon appears with all elements which are closely allied chemically, *e.g.*, neodymium and praseodymium.

Finally, I have still to mention a third group of lines which are strongest in the spectra of the middle fractions; they appear specially clearly on the sensitised plates after a long time of illumination (600 seconds).

To these belong the lines 5104·60, 5067·40, 5009·72, which in the spectra of Ad and Cp show no corresponding marked lines. All these lines indicate that between Ad and Cp a third Yb element exists if in small quantities only. Unfortunately it is hopeless to try to get this element, even in a half pure state. For the separation processes, even supposing that the tendency to separate remained the same, which is not certain, would take many centuries.

To protect myself against claims of priority which have recently been made, I must make a short personal explanation. I proved that ytterbium could be decomposed into two new elements at the beginning of 1905.

In March of the same year I reported this discovery to the Kaiserl. Akademie der Wissenschaften of Vienna. This short but quite positive statement appeared in the academic *Gazette*, No. x., 1905. The following sentences occur in it:—

"It (Yb) consists of two new elements. The spark spectra of the new elements are parts of the spectrum of ytterbium, and this may be regarded as the sum of the two new spectra. Some lines belong to the elements in common."

This report appeared afterwards in many technical papers, and so became widely known.

THE PRESENT STATE OF OUR KNOWLEDGE OF RADIO-ACTIVITY.*

By A. DEBIERNE.

(Concluded from p. 291).

IV.

RADIO-ACTIVE substances were discovered in certain special minerals, and the first researches showed that only minerals containing thorium or uranium are appreciably active. Since these researches extremely sensitive apparatus has been employed, and the presence of active substances has been revealed in a very large number of ordinary materials.

One of the most interesting results was obtained with the mineral waters and the mud deposited by medicinal springs. Extensive experiments by Pierre Curie and Laborde have shown that most mineral waters contain either small quantities of radium or else radium emanation. With some waters the proportion of emanation is fairly large, and it is thought that the curative properties may be due to the presence of the emanation. The researches of Moureu have shown the presence in these waters of helium, neon, and argon which always accompany the emanation.

It has also been proved that the emanation is present in measurable quantities in the atmosphere and in sea-water. Strutt has proved the presence of radium in most minerals, and has performed quantitative experiments, thus determining approximately the amount of radium present on the earth's surface. The result obtained has led to interesting conclusions.

The experiments of Pierre Curie having shown that radio-active transformations are important sources of energy, attempts have been made to find out if the production of energy in the universe may be due to the presence of active substances. It has been found that all the energy emitted by a star such as the sun may be explained by the presence of a relatively small quantity of radium, about 1 grm. per cubic metre.

Since Strutt's determinations enable us to form an approximate idea of the amount of radium on the surface of the earth, we can find out whether the corresponding liberation of heat is appreciable. The following is the result obtained:—

It is known that from a certain depth below the surface of the earth the temperature increases regularly, and determinations have been made of what is called the temperature gradient, *i.e.*, the variation of temperature per unit of length. The existence of a corresponding fall of temperature from the interior of the earth's crust to the exterior results in a continual transference of heat, which can be calculated if the temperature gradient and the mean conductivity for heat of the earth's crust are known. This heat is continually supplied by the interior of the globe, and it must be admitted that the earth is gradually cooling. But not only might the liberation of heat resulting from the presence of radium compensate this loss of heat, but also if it is supposed that the whole mass of the earth contains the same proportion of radium the temperature ought to rise instead of fall. This rise of temperature would be very slow and quite imperceptible.

The study of the phenomena of radio-activity may lead to results of importance in other geological problems. Thus, if we have an accurate knowledge of the mean duration of life of elements such as uranium or thorium, we can form an idea of the age of the minerals which contain them. The age of the minerals might also be calculated approximately by another method—the determination of the quantity of helium they contain, supposing this helium has remained imprisoned in the material. As the law of the production of helium is known approximately the age of the mineral can be deduced. The numbers thus obtained for the radio-active minerals (some hundreds of millions of years) are of the same order of magnitude as those which have been obtained by geologists by other lines of reasoning.

Researches have also been carried out to determine whether the property of radio-activity is limited to certain elements known to us, or whether it is a general property of matter. Such a result is by no means improbable, for we know substances which have very different activities; for instance, radium is several million times more active than uranium, and it is evident that if some substances are only one million times less active than uranium our methods of research would not enable us to detect them. The researches carried out in this direction have shown that space is traversed by a very feeble penetrating radiation, and also that certain ordinary substances appear to possess a true radio-activity. Lead and potassium give decidedly positive results, but it is difficult to decide whether the radio-activity detected is due to the elements themselves or to radio-active impurities.

V.

I will conclude this article by drawing attention to one very important aspect of radio-activity—the regularity and absolute constancy of the laws of the variation of radio-active transformations. It is true that these laws are identical with those which have been deduced for analogous chemical transformations, but they seem absolutely independent of the external conditions. This may be due to the atomic nature of the transformations; however, it is somewhat difficult to form a conception of the mechanism of the phenomenon.

In molecular chemical transformations the progressive transformation of the matter present may be explained by the fact that all the molecules are not in the same state, either owing to collisions with neighbouring molecules or to movements in the interior of the molecule; a molecule does not undergo the transformation in question, which is instantaneous, until, in consequence of these different movements, it reaches a certain state; the progressive law of transformation is a kind of law of chance, which is regular as long as the number of molecules is large and the external conditions remain the same; the same proportion of molecules reaches the state in question during a given interval of time and undergoes the chemical transformation. With radio-active transformations experience shows that external conditions of temperature, &c., have no influence, not even the state of combination; the collisions between the atoms can thus have no influence upon their particular state from the radio-active point of

* *Revue Générale des Sciences*, 1908., xix. 730.

view. The sole remaining possible influence which can intervene are the movements in the interior of the atom. But let us consider a certain quantity of radium C, for example; it may be supposed that at its moment of transformation each atom passes through the same state; this is in agreement with the fact that when an α particle is projected each particle is emitted with the same initial velocity. At the end of three hours almost all the radium C is transformed into radium D. Amongst all the atoms of radium D which start in the same state, at practically the same time, and which, moreover, are not influenced by external agencies—pressure, temperature, state of combination, &c.—some are immediately transformed into radium E, while others may wait for several hundred years before being transformed. In this conception of radio-active transformations there are some points which are difficult of comprehension. Perhaps a better explanation would be reached if it were supposed that the transformation is not absolutely spontaneous, and that an external cause exists for the evolution of the elements, but it is difficult to imagine such a cause.

Finally, it is not impossible that external conditions have a slight influence over the laws of evolution; the experiments which have been performed have up to the present given a negative result, but they have not been numerous, and it cannot be affirmed that we shall not some day succeed in exercising an influence over the production of radio-active transformations.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

Part III.—Analysis of the Aluminium and Iron Groups, including Beryllium, Uranium, Vanadium, Titanium, Zirconium, and Thallium.

By ARTHUR A. NOYES, WILLIAM C. BRAY, and ELLWOOD B. SPEAR.

(Continued from p. 292).

Confirmatory Experiments and References (continued).

Behaviour of Vanadyl Salts and Vanadic Acid towards Potassium Ferrocyanide.—5 mgrms. V as Na_3VO_4 after evaporation with HCl (whereby it is reduced to vanadyl chloride) were treated by *P. 58*d*; a greenish yellow precipitate separated. The precipitate was filtered off, and the filtrate tested for vanadium by *P. 58*e*; only a very faint pink colour resulted, showing that the precipitation of the vanadium by the ferrocyanide is nearly complete. The experiment was repeated except that only two drops of HCl were added and the solution was not evaporated; no precipitate separated in half an hour, showing that a small quantity of vanadium in the form of vanadic acid is not precipitated by $K_4Fe(CN)_6$.

*P. 58*e*: *Non-interference of Lead with the Vanadium Test.*—A solution containing 2 mgrms. Pb as $Pb(NO_3)_2$, and 0·5 mgrm. V as Na_3VO_4 and 2 grms. NH_4NO_3 was treated by P. 58*e*, and the black precipitate of PbS formed was filtered off; on saturating completely with H_2S, the filtrate had the characteristic violet-red colour due to vanadium.

*P. 58*g*, N. 1: *Separation of Aluminium and Beryllium.*—See Havens (*Zeit. Anorg. Chem.*, 1898, xvi., 15).

Precipitation of Aluminium as $AlCl_3.6H_2O$.—0·5 mgrm. Al as $AlCl_3$ was treated by *P. 58*g*, the total volume of the acid ether mixture being about 15 cc.; on saturating with HCl gas no precipitate could be seen, but on standing about fifteen minutes a distinct crystalline precipitate separated out.

100 and 500 mgrms. Al as $AlCl_3$ were treated by *P. 58*g*; the filtrates, which had a total volume of about 70 cc., were evaporated to about 20 cc. and made alkaline with NH_4OH; no precipitate separated, but in the second experiment there was a faint turbidity corresponding perhaps to 0·1 mgrm. Al.

Behaviour of Beryllium, Uranium, and Chromium in the Hydrochloric Acid Ether Process.—100 mgrms. Be as $BeCl_2$ were treated by *P. 58*g*, the final volume being about 30 cc.; a small precipitate remained. This was filtered off, washed twice, dissolved in a little water, and proved to contain aluminium but no beryllium by boiling in a 10 per cent $NaHCO_3$ solution as described in *P. 58*h*.

500 mgrms. Al and 2 mgrms. Be as chlorides were treated by *P. 58*g* in a volume of 60 cc., and the filtrate was treated by *P. 58*h*; a good test for beryllium was obtained, and the amount of beryllium in the filtrate was estimated to be 1 or 2 mgrms., showing that very little beryllium was retained by the $AlCl_3.6H_2O$.

100 mgrms. U as UO_2Cl_2 were treated by *P. 58*g*, the total volume being 50 cc.; a clear yellow solution was obtained.

20 mgrms. Cr as K_2CrO_4 were boiled with HCl (1·20) to reduce the chromium to the chromic state, and the green solution was treated by *P. 58*g*, in a volume of about 30 cc.; the green colour quickly disappeared and a violet precipitate separated. This was filtered off after several hours and the filtrate tested for chromium by evaporating, adding NH_4OH, and boiling; a precipitate estimated to contain 5—10 mgrms. Cr separated.

*P. 58*h*, N. 1: *Separation of Beryllium and Aluminium in Strong Sodium Hydrogen Carbonate Solution.*—See Parsons and Barnes (*Journ. Am. Chem. Soc.*, 1906, xxviii., 1589).

200 mgrms. Al as nitrate were dissolved in 20 cc. water, and added to a warm solution of 10 grms. $NaHCO_3$ in 80 cc. water; the mixture was heated to boiling in a flask, boiled for one minute, and filtered; the filtrate was acidified with HNO_3, evaporated to about 20 cc., and made alkaline with NH_4OH; no precipitate separated on warming gently, nor on standing.

100 mgrms. Al and 1 mgrm. Be as nitrates were dissolved in 50 cc. water and 6 grms. $NaHCO_3$ were added; the mixture was heated to boiling, boiled for one minute, and filtered while still hot; the filtrate was made acid with HNO_3, evaporated to about 10 cc., and made alkaline with NH_4OH; a very small precipitate separated, which was estimated to contain 1/20 mgrm. Be. The experiment was repeated with 2 mgrms. Be; the result was the same. The experiment was repeated with 5 mgrms. Be; scarcely 1 mgrm. Be was found in the filtrate. Therefore small amounts of beryllium cannot be completely separated from 100 mgrms. Al by this method.

The precipitate obtained in the experiment with 1 mgrm. Be was treated by *P. 58*g*—*h*; the beryllium present was estimated to be nearly 1 mgrm., showing that this separation with HCl and ether is more satisfactory than that with 10 to 12 per cent $NaHCO_3$.

Behaviour of Iron in Strong Sodium Hyarogen Carbonate Solution, and its Precipitation as Sulphide.—2 and 5 mgrms. Fe as $FeCl_3$ were treated by the last paragraph of *P. 58*h*; small precipitates of $Fe(OH)_3$ were formed in the $NaHCO_3$ solutions, but the precipitation was incomplete, for after acidifying the filtrates and adding NH_4OH, precipitates of $Fe(OH)_3$ were obtained, each of which was estimated to contain over 1 mgrm. Fe. The experiment with 5 mgrms. Fe was repeated except that 5 cc. NaOH were added to the $NaHCO_3$ filtrate; no precipitate resulted in the cold, but about 0·5 mgrm. Fe as $Fe(OH)_3$ precipitated on boiling. The precipitation was still incomplete for about 0·5 mgrm. Fe was found in the solution on acidifying and adding NH_4OH.

0·5 mgrm. Fe as $FeSO_4$, and in a second experiment as $FeCl_3$, was boiled with 30 cc. 10 per cent $NaHCO_3$, for one minute, the mixtures were poured through filters, cooled, and H_2S was passed in for about three seconds; the solutions became dark coloured at once. After about five minutes the mixtures were filtered; the filtrates were clear, with a faint greenish shade corresponding to an insignificant amount of iron; more H_2S caused no further

* From the *Journal of the American Chemical Society*, xxx., No.4.

darkening. The experiment with 0·5 mgrm. Fe as $FeCl_3$ was repeated, except that the $NaHCO_3$ solution was not cooled before passing in H_2S; a dark green solution was obtained which ran through the filter, showing that it is better to add the H_2S in the cold. To this solution (which was now cold) was added 2 or 3 mgrms. Fe as $FeSO_4$; on filtering after several minutes the filtrate was nearly colourless, and more H_2S gave no precipitate nor colour.

*P. 58*h*, N. 2: *Behaviour of Uranyl Salts in Strong Sodium Hydrogen Carbonate Solution, and on Passing in* H_2S.—50 mgrms. U as UO_2Cl_2 (and in another experiment as $UO_2(NO_3)_2$) were dissolved in a little water and added to a solution containing 5 grms. $NaHCO_3$, the final volume being 50 cc.; the mixture was boiled for five minutes; no precipitate separated. The experiment was repeated with 5 mgrms. U as UO_2Cl_2 in a volume of 30 cc. and 10 cc. 10 per cent NaOH was added to the 10 per $NaHCO_3$ solution after boiling; no precipitate separated.

To a mixture containing 100 mgrms. Be and 20 mgrms. U dissolved in 50 cc. 10 per cent $NaHCO_3$ was added 1 grm. NH_4Cl, and the mixture was boiled; no precipitate separated.

A mixture containing 100 mgrms. Be and 10 mgrms. U (but no iron) dissolved in 30 cc. 10 per cent $NaHCO_3$ solution was saturated completely with H_2S gas; no precipitate separated.

The Separation of Uranium and Beryllium by Potassium Ferrocyanide.—15 and 25 mgrms. Be as chlorides in HCl solution were evaporated almost to dryness, 10 cc. saturated NaCl solution added, the mixture was cooled and 5 cc. 10 per cent $K_4Fe(CN)_6$ solution were added; clear solutions resulted which were blue coloured, owing to the presence of a small amount of iron in the beryllium; after standing several hours a gelatinous light coloured precipitate had separated in the experiment with 25 mgrms. Be. The experiment was repeated with mixtures of 1 mgrm. U as $UO_2(NO_3)_2$, and with 5, 10, 15, and 20 mgrms. Be; a dark red colour appeared at once in the experiments with 5 and 10 mgrms. Be, and on standing dark red precipitate settled out. In the experiments with 15 and 20 mgrms. the colour was somewhat obscured owing to the presence of the iron. The experiment with 20 mgrms. Be and 1 mgrm. U was repeated, except that the iron was first removed from the beryllium solution by P. 52; a good test for uranium was then obtained.

P. 61, N. 1: *Solubility of Manganic Peroxide in* HNO_3 *in the Presence of Filter-paper.*—500 mgrms. Mn as $Mn(NO_3)_2$ were treated by P. 52; the $MnO(OH)_2$ precipitate was boiled with 30 cc. HNO_3 (1·20) in a covered casserole for several minutes; very little of the precipitate dissolved. The experiment was repeated except that the filter, as well as the precipitate, was treated with the nitric acid; on boiling, the filter disintegrated and the precipitate dissolved completely in ten or fifteen minutes. The last experiment was repeated with HNO_3 (1·42); nearly all of the precipitate dissolved after five minutes' boiling, and the remainder on standing over night. The solution obtained in the last experiment was evaporated to a small volume and diluted to about 15 cc.; the paper was filtered off, and the filtrate was treated by P. 61; the manganese was completely precipitated.

P. 62, N. 2: *Precipitation of Manganese by Chloric and Nitric Acids.*—See Hannay (*Journ. Chem. Soc.*, 1878, xxiii., 269); Ford (*Trans. Inst. Min. Eng.*, ix., 397).

P. 62, N. 3: *Separation of Other Elements from Manganese by Chloric and Nitric Acids.*—See T. A., Nos. 117, 118.

Iron.—100 mgrms. Mn as $MnCl_2$ and 1 mgrm. Fe as $FeSO_4$ were treated by P. 52 and P. 61, and the filtrate was tested for iron by P. 64; a good test was obtained. 500 mgrms. Mn as $MnCl_2$ and 1 mgrm. Fe were treated by P. 52 and then by P. 61; the precipitate and filtrate were tested for iron by evaporating with excess of HCl, diluting, and adding KSCN solution; a distinct test for iron was obtained in the filtrate, but much more iron was found in the precipitate than in the filtrate.

Titanium.—A mixture containing 500 mgrms. Mn and 1 mgrm. Ti as nitrates was treated by P. 61; the filtrate was evaporated and made alkaline with NH_4OH; no precipitate separated, proving that the titanium had been completely carried down with the MnO_2. This experiment was repeated with 5 and with 50 mgrms. Ti; the result was the same in each case. The experiment was repeated with 50 mgrms. Mn and 50 mgrms. Ti; the precipitate was analysed by *P. 62*a*, and about half the titanium found in it; the filtrate was evaporated almost to dryness; some of the titanium separated during the evaporation as a white precipitate, which did not dissolve readily in HCl, but did in HF. The experiment was repeated with 50 mgrms. Ti in the absence of manganese; no precipitate separated on adding $KClO_3$, nor on evaporating to 5 or 10 cc.

Zirconium.—A mixture containing 500 mgrms. Mn and 2 mgrms. Zr as nitrates was treated by P. 61; the filtrate was evaporated and made alkaline with NH_4OH; only a very small precipitate separated, showing that not quite all of the zirconium had been carried down. The experiment was repeated with 50 mgrms. Zr; the filtrate was found to contain 15 or 20 mgrms. Zr. The manganese precipitate was treated by *P. 62*a*; the rest of the zirconium was recovered.

Vanadium.—A mixture containing 250 mgrms. Mn as nitrate and 1 mgrm. V as Na_3VO_4 was treated by P. 61; the filtrate was treated by *P. 58*e* to test for vanadium; no trace of vanadium was found. For the fact that vanadium is not carried down by manganese in the Na_2O_2 procedure see C. E., P. 52, N. 11. The experiment was repeated with 250 mgrms. Mn and 10 mgrms. V; a mere trace of vanadium was found. The experiment was repeated with 50 mgrms. Mn and 10 mgrms. V; not more than 1 or 2 mgrms. V were found in the filtrate. The experiment was repeated with 20 mgrms. Mn and 10 mgrms. V; the filtrate contained not more than 2 or 3 mgrms V.

Uranium.—A mixture of 250 mgrms. Mn as $Mn(NO_3)_2$ and 1 mgrm. U as $UO_2(NO_3)_2$ was treated by P. 61; the filtrate was tested for uranium by *P. 58*d*; a good test for uranium was obtained.

Thallium.—15 mgrms. Tl as $Tl(OH)_3$ were treated by P. 61; no precipitate separated. 200 mgrms. Mn as $MnCl_2$ and 1 mgrm. Tl as $TlCl_3$ were treated by this procedure. The filtrate was tested for thallium by the regular procedure; a good test was obtained. The precipitate was dissolved in HCl (1·12) and treated by *P. 65*a*—*d*; a very small precipitate of TlI was obtained, which was estimated to contain not more than 0·1 mgrm. Tl, showing that thallium is not carried down with the manganese.

The Test for Titanium with H_2O_2 *in the Presence of Iron, Cobalt, or Nickel.*—500 mgrms. Fe as $FeCl_3$ were evaporated with a large excess HNO_3 (1·42) to 5 cc.; the dark red solution was diluted to 40 cc.; it became almost colourless. The solution was divided into two parts, and to one of these 0·5 mgrm. Ti as $TiCl_4$ solution was added; to both parts 2 or 3 cc. H_2O_2 were added; in both a deep yellow colour very clearly indicated the presence of titanium. The experiment was repeated, except that the HNO_3 solution was diluted to about 15 cc.; the test for titanium was distinct, although the ferric solution was not quite colourless.

500 mgrms. Co as $Co(NO_3)_2$ were evaporated with excess HNO_3 (1·42) to 5 cc.; the red solution was diluted to 15 cc. and divided into two parts, to one of which 1 mgrm. Ti was added; 2 cc. 3 per cent H_2O_2 were added; the solution containing titanium acquired a reddish colour of a distinct yellow tinge.

The experiment was repeated with 500 mgrms. Ni as $Ni(NO_3)_2$; the green colour of the nickel solution containing titanium changed to olive when the H_2O_2 was added.

P. 62, N. 1: *Confirmatory Test for Manganese with Lead Dioxide.*—To 1 grm. PbO_2 and 10 cc. HNO_3 (1·20) in a casserole were added in separate experiments 0·5, 0·2, 0·1, and 0·02 mgrm. Mn as $MnCl_2$. The mixtures were boiled gently for about two minutes, in covered casseroles, and then poured into test-tubes; after the PbO_2 had settled the colour of $KMnO_4$ could be clearly seen, even in the last experiment. The experiment was repeated without adding $MnCl_2$; a perfectly colourless solution was obtained. The series of experiments was repeated, except that HNO_3 (1·42) was used; the colour of $KMnO_4$ was easily distinguished in each case, but was not so pronounced as with the more dilute acid. Moreover, on standing the pink colour faded slowly in the concentrated HNO_3.

To determine whether the test would be satisfactory when the manganese was initially present as MnO_2, 1 mgrm. Mn as $MnCl_2$ was treated by P. 61, and the precipitate collected on an asbestos filter. About one-tenth of it (*i.e.*, 0·1 mgrm. Mn) was treated by P. 62; the permanganate colour was very distinct.

*P. 62*a*, N. 1: *Separation of Titanium and Zirconium from Manganese by Ammonia.*—To a mixture containing 50 mgrms. Mn and 50 mgrms. Ti as nitrates, and 4 cc. HCl (1·12) in 50 cc. was added NH_4OH (0·96) very carefully until the mixture was barely alkaline to litmus-paper; a white precipitate formed. Two drops more NH_4OH (0·96) were added, and the mixture was heated on a steam-bath for ten minutes; the precipitate remained white. The solution was filtered. The filtrate was tested for titanium by adding more ammonia; no more precipitate separated at once, showing that the precipitation of the titanium was complete. The precipitate was dissolved in hot HCl, the process was repeated, and the filtrate was tested for manganese by adding $(NH_4)S_2$; a precipitate estimated to contain 3 or 4 mgrms. Mn separated. The titanium precipitate was again dissolved and treated in the same way; no manganese was found in the filtrate, showing that the manganese had been completely removed in two separations. The experiment was repeated except that the two drops of ammonia in excess were not added; only about two-thirds of the titanium precipitated. The experiment was repeated, except that NH_4OH was added until the odour after shaking was distinct; the NH_4OH precipitate was brown, showing the presence of a large amount of manganese. The last experiment was repeated, except that 15 grms. NH_4Cl were also added; the NH_4OH precipitate was white, and contained only about 1 mgrm. Mn. These experiments prove that a satisfactory separation is obtained only when the hydroxide-ion concentration is very small.

A solution containing 500 mgrms. Mn and 1 mgrm. Ti as nitrates, and 10 cc. HCl (1·12) in 60 cc., was made barely alkaline to litmus-paper by means of NH_4OH (0·96), an excess of two drops NH_4OH was added, and the mixture was heated for ten minutes on a steam-bath; the precipitate was dark coloured. The precipitate was dissolved in hot HCl and the separation repeated; a small white precipitate resulted, which was practically free from manganese. It was dissolved in HCl, and a little 3 per cent H_2O_2 was added; the solution became deep yellow, showing the presence of titanium. The experiment was repeated with 500 mgrms. Mn and 2 mgrms. Zr as nitrates; the results were the same. The final white precipitate was dissolved in hot HCl, the solution was evaporated to a few drops, and a piece of turmeric-paper was dipped in it and dried over a small flame; it turned pink, proving the presence of zirconium.

Separation of Zirconium from Manganese by Ammonium Acetate.—A solution of 500 mgrms. Mn and 5 mgrms. Zr in 10 cc. HCl (1·12) was just neutralised with NH_4OH; 2 cc. 30 per cent acetic acid were added, the mixture was diluted to 50 cc., 6 cc. 50 per cent ammonium acetate were added, and the mixture was boiled; the precipitate was brown, showing that several mgrms. of manganese were present and that the separation was unsatisfactory.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

Ordinary Meeting, November 27th, 1908.

Dr. Charles Chree, F.R.S., President, in the Chair.

The President announced that the Council had appointed Mr. S. W. J. Smith to succeed the late Prof. Cassie as an Honorary Secretary of the Society.

Mr. R. L. Jones was elected a Fellow of the Society.

A paper entitled "*A Graphic Method of dealing with Refracting Surfaces*" was read by Mr. H. S. Allen.

In this paper a graphic method is given for finding the cardinal points for combinations of coaxial refracting surfaces. The method may be applied to such cases as that of two thin lenses a finite distance apart, two refracting surfaces forming a thick lens, or to the general case of the combination of two lens systems. Through the second focal point of the first system, set off a line $F_1'E_1$ at right angles to the axis, equal to the second focal length of that system. Draw F_2E_2 similarly through the first focal point of the second system equal to the first focal length of that system. F'_1E_2 and F_2E_1 intersect in C a point in the plane of the optic centre of the combination. The images of C formed by the two systems determine the principal planes of the combination. By tracing the rays CE_1 and CE_2 through each system a simple construction is obtained for the cardinal points and focal lengths. The method avoids the use of continued fractions, and may be of value for investigating the way in which the properties of a combination are affected by making given alterations in the character or separation of the components. It affords non-mathematical students a means of realising the existence of the cardinal points for a complicated system of refracting surfaces.

Dr. Eccles remarked that the author's treatment of refracting surfaces was limited to spherical surfaces and to the direct incidence of pencils of infinitesimal aperture. If the treatment were extended to the discussion of oblique pencils and the construction of caustics it would be very valuable. The author's method, as developed to the present, consisted of applying the well-known graphical construction for a harmonic mean, to the successive lenses or spherical surfaces met with in the coaxial system of lenses or surfaces under consideration. Now the harmonic construction just mentioned is a particular case of the general graphical connection between two collinear projective (or homographic) ranges of points; and therefore the speaker preferred, in his own teaching of geometrical optics, to use general projective constructions rather than this harmonic construction. As a fact, the general projective method would be felt to be the easier of the two, by any one familiar with the fundamental principles of projective geometry, or, as it is sometimes called, "geometry of position." From the point of view of projective geometry the object-points and the image-points on the axis of a refracting (or reflecting surface), since they have a true one-one correspondence (as shown by their algebraic homographic connection), constitute two collinear projective ranges of points. Two such ranges can be graphically correlated, it is known, by at most three projections. The rays used in the first and last of these projections may be interpreted optically as rays of light through a source of light and through its image. The intermediate projection gives the central point on which the author lays stress. If this point be taken at infinity the planes of unit magnification become defined. Since any number of successive projections at successive surfaces leave the ultimate range of image-points homographic with the original range of object-points, it is proved that any lens system whatever of the kind specified by the author can be summarised graphically by three projections. Moreover, no graphical construction can be

obtained which is not comprehended in the general projective method just sketched. In treatises on projective geometry the properties of these projective ranges and pencils are demonstrated, and they need merely be translated into optical language to give many beautiful and powerful graphical optical theorems. There is reason to think that caustics can be approached along these lines. The speaker expressed the hope that the author would devote still further effort to these much desired simplifications of geometrical optics.

Dr. A. Russell congratulated the author, and indicated a simple graphical method of determining the focal length of two thin lenses in contact when the focal length of each was known.

Prof. C. H. Lees thought the graphical method described by the author was an improvement upon algebraic methods.

A paper on "*An Accurate Method of Measuring Moments of Inertia*," by the late Prof. W. Cassie, was read by the President.

In this method use is made of the periods of small oscillations of a balance-beam. The method consists in taking as standard moment of inertia a known mass hung from the knife-edge of a balance and comparing others with it. The time of swing is taken with the standard mass in one pan and a counterpoise in the other. The body whose moment of inertia is required is attached to the beam in such a manner that the coefficient of the directive couple is unaltered and the time of swing is determined without weights in the pans. From these times, with a knowledge of the length of the beam and the masses used, the moment of inertia required is easily calculated. In the paper the method of attaching the body of unknown moment of inertia to the balance-beam is described fully.

The Secretary read a letter from Prof. W. Stroud describing a method of determining moments of inertia in use in the University of Leeds. In this method two vibrators perpendicular to one another are used, and they can be arranged to produce a Lissajou figure. The horizontal vibrator carries a vertical slit and *vice versa*; and as the two slits are placed one behind the other, a small spot of light can be seen through the combination. The vertical vibrator consists of a stout metal framework supported by a torsion wire, and carrying a platform upon which the body whose moment of inertia is required can be placed. The time of swing of this vibrator is then adjusted (by the addition of rings of known moment of inertia) to be equal to that of the horizonal vibrator, so that the Lissajou figure is invariable. The body is then placed upon the platform, and inertia rings are removed till the Lissajou figure is reproduced or nearly so. Then, accurate observations are taken of the number of oscillations required to complete a cycle with inertia rings slightly below and slightly above the correct value, which is got by interpolation. The vibrators are kept in continuous oscillation by an electromagnetic make and brake.

Prof. C. H. Lees said that Prof. Stroud's method did not seem capable of giving very accurate results on account of want of homogeneity of the rings.

Dr. A. Russell asked if it was necessary to take account of changes in barometric pressure in accurate work on moments of inertia.

The Chairman remarked that in delicate work attention must be paid to the effects of changes in barometric pressure.

Mr. S. Russ read a paper "*On the Diffusion of Actinium and Thorium Emanations*."

Experiments were described in which the emanation of actinium was allowed to diffuse into the following gases:—Air, hydrogen, carbon dioxide, sulphur dioxide, and argon. The diffusion coefficients of the emanation in these gases agree in general with those calculated by means of Graham's Law, making use of the diffusion coefficient in air, The variation with pressure of the diffusion coefficient of the actinium emanation in air was shown to be quite in accordance with the ordinary gas laws, down to a few centimetres pressure; the product the pressure and diffusion cofficient remaining practically constant. Experiments under identical experimental conditions with thorium emanation over a similar range of pressure also yield nearly a constant value for the product of pressure and diffusion coefficient. The ratio of the two constants thus obtained leads directly to a ratio of the molecular weights of the two emanations, the result being that thorium emanation appears to have about 1·4 times the molecular weight of actinium emanation.

Prof. C. H. Lees pointed out that the low values for the molecular weights of the emanations had all been obtained by allowing the emanations to diffuse into light gases. Prof. Pickering had allowed them to diffuse into mercury vapour, and obtained a value about 230.

A paper, "*On the Elliptic Polarisation produced by the Direct Transmission of a Plane Polarised Stream through a Plate of Quartz cut in the Direction Oblique to the Optic Axis, with a Method of determining the Error of a Plate supposed to be Perpendicular to the Axis*," by Mr. J. Walker, was taken as read.

When a stream of light polarised in an azimuth α with respect to the principal section traverses a plate of quartz cut obliquely to the optic axis, the polarisation of the emergent stream is given by equations (3), in which $\tan\gamma$ is the ratio of the elliptic vibrations and θ determines the azimuth of the plane of maximum or minimium polarisation, according as γ is numerically less or greater than $\pi/4$; the quantities R, Δ occurring in these equations are connected with the ellipticity of the polarisation of the streams of permanent type within the crystal and the relative retardation, δ, introduced by the passage of equations (1).

Expressing $\tan(\theta - \alpha)$ and $\sin 2\gamma$ in terms of $\tan R$, we find that they both take the form—

$$\frac{2(a\tan R + b\tan^2 R}{1 + c\tan^2 R},$$

the maximum and minimum values of which are $a\tan R_m$, occurring when—

$$\tan R = \tan R_m = \frac{b \pm \sqrt{b^2 + a^2 c}}{ac}.$$

From these equations the changes in the character of the emergent stream may be traced as R increases through a half period, corresponding to the variation of δ through a complete period.

Writing $\tan\psi = \tan 2\alpha/\sin 2\beta$, it may be noted that the emergent light is plane polarised in the primitive plane when $\delta = 2n\pi$, and is again plane polarised in a plane symmetrical to the primitive plane with respect to the principal section when $\delta = (2n+2)\pi - 2\psi$, and that $\sin 2\gamma$ attains its maximum and minimum values when $\delta = (2n+1)\pi - \psi$ and $(2n+2)\pi - \psi$. Also that $\sin 2\gamma$ can only become numerically equal to unity, if—

$$\cos 2\alpha = \pm\tan 2\beta,$$

and hence, except in these cases, θ always gives the plane of maximum polarisation and the light is never circularly polarised.

On the other hand, maximum and minimum values of $\tan 2(\theta - \alpha)$ only occur, if $\cos^2 2\alpha > \tan^2 2\beta$, and when this is the case, writing—

$$\cos^2 2\alpha - \tan^2 2\beta = \cos^2\chi,$$

these values are $\tan(\chi - 2\alpha)$ and $-\tan(\chi - 2\alpha)$.

Thus as R increases the plane of maximum polarisation rotates continuously, if $\cos^2 2\alpha < \tan^2 2\beta$, while if $\cos^2 2\alpha > \tan^2 2\beta$ it oscillates between two extreme positions.

This is a generalisation of a condition given by Monnory for the special case in which $\alpha = 0$. When $\cos^2 2\alpha = \tan^2 2\beta$, θ increases by a right-angle only, as δ changes by a complete period; the light is circularly polarised when $\tan R = \cot 2\alpha$, and while for values for R less than that given by this equation, θ gives the plane of maximum polarisation, for greater values it determines the plane of minimum polarisation.

In § 6 the expression is obtained for the intensity when the light is analysed in any azimuth, and the result is applied to the case in which white light passes and is subsequently examined with a spectroscope—an investigation rendered necessary by the difference in the accounts of the phenomenon given by Cruellebois and Beaulard. If the light emergent from the quartz be investigated with a Savart's analyser, it is clear that the bands will only disappear when the light is plane polarised in a plane parallel to the principal section of either plate of the analyser. Now it is shown in an early part of the paper that the light on leaving the quartz is plane polarised (1) in the primitive plane, when $\delta = 2n\pi$, (2) in a plane making an angle $n\pi - \alpha$ with the principal section, when—

$$\tan \frac{\delta}{2} = -\tan 2\alpha / \sin 2\beta.$$

It thus follows, that if the light be initially polarised in a plane parallel to the principal section of either plate of analyser, *i.e.*, in a plane such that the bands disappear when the quartz plate is away, there will be a disappearance of the bands when $\delta = 2n\pi$, and that if the principal section of the quartz plate bisect the angle between the principal sections of the Savart's compound plate, there will be in addition a further disappearance of the bands whenever $\delta = (2n + 1)\pi$.

This leads to a method of determining the error of a plate supposed to be perpendicular to the optic axis, that is described at the end of the paper.

A paper by Mr. W. C. M. Lewis, entitled "*An Experimental Investigation of Gibbs's Theory of Surface-concentration regarded as the Basis of Adsorption*," was taken as read.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvii., No. 19, November 9, 1908.

Products of the Reaction of Sodamide on Ketones.—A. Haller and Ed. Bauer.—When a benzene or toluene solution of benzophenone is boiled with sodamide, a copious white precipitate is formed, sometimes preceded by an intense blue coloration, and the sodamide slowly dissolves with or without the formation of a deposit. The coloration is undoubtedly due to the action of small quantities of sodium, retained by the amide, on benzophenone, for when no alkali metal is present sodamide gives no coloration with benzophenone; moreover, sodium alone, when heated with benzophenone, gives an intense coloration. The white precipitate is not formed when an absolutely anhydrous solvent is employed; if it is not formed at once the addition of a few drops of water will hasten its appearance. The precipitate seems to consist of a sodium amido compound of benzophenone of formula—

$$C_6H_5C\begin{matrix}\diagup ONa \\ \diagdown NH_2\end{matrix}C_6H_5.$$

The reactions are—

$$C_6H_5.CO.C_6H_5 + NH_2Na = C_6H_5.C\begin{matrix}\diagup ONa \\ \diagdown NH_2\end{matrix}C_6H_5,$$

$$C_6H_5.C\begin{matrix}\diagup ONa \\ \diagdown NH_2\end{matrix}C_6H_5 + H_2O = C_6H_5CONH_2 + C_6H_6 + NaHO.$$

This seems to be a general reaction for all aromatic ketones; anthraquinone, however, does not give it.

Ionisation by Phosphorus and Phosphorescence.—Léon and Eugène Bloch.—By means of a current of gas the phosphorescence may be separated from phosphorus by a perfectly dark space. The phosphorus sometimes retains a slight phosphorescence, but this may be altogether extinguished by increasing the flow of gas. The authors experiments show that phosphorescence, ionisation, and ozone are all formed in the same region, which may be separated from the element when the current of gas is rapid enough. This shows that these phenomena are not produced by the direct oxidation of solid phosphorus, but by the oxidation of a substance which emanates from the phosphorus and is carried away by the current of gas. This substance is very probably phosphorous anhydride. If a current of gas is passed rapidly enough through a tube containing phosphorus to render it perfectly dark, and is then suddenly cut off, phosphorescent specks are seen. They disappear when they come in contact with one another. This phenomenon may be explained by supposing that the dark tube contains unoxidised phosphorous anhydride which is spontaneously inflammable. Hence phosphorescence, ionisation, and formation of ozone are not due to the oxidation of phosphorus, but of phosphorous anhydride.

True Atomic Weight of Silver from Stas's Experiments.—Louis Dubreuil.—Generally speaking, it is impossible to deduce the true value of an atomic weight by determining a single analytical ratio. The application of the method of the least squares enables the most probable value of all the atomic weights found in each experiment to be calculated. By comparing the values thus obtained the true atomic weight can be deduced, the number being more accurate the greater the number of methods employed. Applying these principles to the case of silver it is found that the true atomic weight does not differ from 108 by more than +0·0079.

Alloys of Silicon and Silver.—G. Arrivaut.—The author has investigated the formation of compounds of silicon with silver by Tammann's method of thermic analysis. He finds that the curve of the liquid phase is composed of two branches, starting from the melting-points of silicon (1415°) and silver (950°) respectively, and cutting at 800°, at a point corresponding to a mixture containing about 5 per cent of silicon. The curve of the solid phase consists of a straight line passing through the eutectic point, and reaching from 0 to 90 per cent of silicon. Thus, silicon and silver form no compound. As to the miscibility in the solid state the duration of eutectic crystallisation points to the existence of mixed crystals of silicon and silver saturated from 10 per cent of silver.

Identity of Ilicic Alcohol with α-Amyrine.—E. Jungfleisch and H. Leroux.—The identity of ilicic alcohol with α-amyrine may be proved by the comparison of the physical properties of the two substances and of their acetic and benzoic ethers. The benzoate is dimorphous, existing as long silky needles and also in the form of prisms. A mixture of the two forms can exist for several days, but the prismatic form seems to increase slowly at the expense of the other.

New Method of Cyclisation of α-Methyl Sparteïn.—Amand Valeur.—α-Methyl sparteïn readily fixes bromine and iodine, the fixation in the case of iodine being accompanied by an isomerisation. In diiodo-α-methyl sparteïn one of the iodine atoms is attached to the nitrogen, and hence the compound is the iodomethylate of an iodated base. The reduction of the diiodo-compound gives the iodomethylate of isosparteïn, and hence the former is the iodomethylate of iodoisosparteïn.

TO CORRESPONDENTS.

G. J. Woods.—Chrome alum dissolves in about 6 or 7 parts of cold water. Consult A. M. Comey's "Dictionary of Chemical Solubilities," published by Macmillan and Co.

MEETINGS FOR THE WEEK.

Monday, 21st.—Faraday Society, 8. "Influence of Cheap Electricity on Electrolytic and Electrothermal Industries," by E. A. Ashcroft.

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THE CHEMICAL NEWS.

Vol. XCVIII., No. 2561.

ON SCANDIUM.*

By Sir WILLIAM CROOKES, D.Sc., F.R.S.

(Concluded from p. 297).

Scandium Ortho-toluate,

$\left(C_6H_4<\begin{matrix}CH_3\\COO\end{matrix}\right)_2ScOH,3H_2O =$

$= (C_8H_7O_2)_2ScOH,3H_2O = C_{16}H_{15}O_5Sc,3H_2O.$

When scandium hydroxide is boiled with an excess of aqueous ortho-toluic acid, a salt is formed with the composition given above. It is a white crystalline powder insoluble in water.

The same salt is formed by mixing solutions of ammonium ortho-toluate and scandium nitrate. It forms a voluminous white curdy precipitate, insoluble in hot or cold water. It contains 3 molecules of water, which are not driven off at 150°.

Analysis.

12·316 grs. of scandium ortho-toluate dried *in vacuo* over sulphuric acid left on ignition 2·171 grs. of scandia, = 1·4059 grs. of scandium.

		Theory.		Experiment.
Sc		44·100	11·45	11·42
C_{16}	192·000			
H_{15}	15·120	341·168	88·55	88·58
O_5	80·000			
$3H_2O$	54·048			
		385·268	100·00	100·00

It is seen that this ortho-toluate has the same percentage composition as the phenyl-acetate, but differs in structural constitution.

Basic Scandium Ortho-toluate.

When scandium hydroxide is boiled with solution of ortho-toluic acid, keeping the hydroxide in slight excess, a basic scandium ortho-toluate is formed. It can be decanted easily from the excess of hydroxide, which is of greater density; it is anhydrous and has the composition—

$$2C_6H_4<\begin{matrix}CH_3\\COOScO\end{matrix} + Sc(OH)_3 = 2C_8H_7O_3Sc + Sc(OH)_3.$$

This basic ortho-toluate is a white powder, insoluble in water and alcohol, but easily soluble in dilute acids.

Analysis.

1. 6·402 grs. of basic scandium ortho-toluate, dried over sulphuric acid *in vacuo*, left on ignition 2·711 grs. of scandia, = 1·7556 grs. of scandium.
2. 7·631 grs. of basic scandium ortho-toluate left on ignition 3·219 grs. of scandia, = 2·0846 grs. of scandium.

		Theory.		Experiment.	
				1.	2.
Sc_3		132·300	27·25	27·42	27·32
C_{16}	192·000				
H_{17}	17·136	353·136	72·75	72·58	72·68
O_9	144·000				
		485·436	100·00	100·00	100·00

* A Paper read before the Royal Society, April 30, 1908.

The above basic salt is formed by the union of two molecules of the ortho-toluate, $C_8H_7O_3Sc$, with one molecule of scandium hydroxide, $Sc(OH)_3$.

Scandium Meta-toluate,

$\left(C_6H_4<\begin{matrix}CH_3\\COO\end{matrix}\right)_2ScOH,3H_2O =$

$= (C_8H_7O_2)_2ScOH,3H_2O = C_{16}H_{15}O_5Sc,3H_2O.$

This salt is formed by double decomposition between ammonium meta-toluate and scandium nitrate solutions. It comes down as a voluminous white curdy precipitate, insoluble in water.

Analysis.

15·702 grs. of the meta-toluate, dried *in vacuo* over sulphuric acid at the ordinary temperature, left on ignition 2·673 grs. of scandia, = 1·7310 grs. of scandium.

		Theory.		Experiment.
Sc		44·100	11·45	11·02
C_{16}	192·000			
H_{15}	15·120	341·168	88·55	88·98
O_5	80·000			
$3H_2O$	54·048			
		385·268	100·00	100·00

Scandium Para-toluate,

$\left(C_6H_4<\begin{matrix}CH_3\\COO\end{matrix}\right)_2ScOH,3H_2O =$

$= (C_8H_7O_2)_2ScOH,3H_2O = C_{16}H_{15}O_5Sc,3H_2O.$

Scandium para-toluate is formed by double decomposition in the same manner as the ortho-toluate, and has the same composition. It separates with three molecules of water, which are not driven off at 150°. It is a white curdy precipitate insoluble in hot or cold water.

Analysis.

12·332 grs. of scandium para-toluate on ignition left 2·141 grs. of scandia, = 1·3865 grs. of scandium.

		Theory.		Experiment
Sc		44·100	11·45	11·24
C_{16}	192·000			
H_{15}	15·120	341·168	88·55	88·76
O_5	80·000			
$3H_2O$	54·048			
		385·268	100·00	100·00

Scandium Phenyl-acetate,

$(C_6H_5CH_2COO)_2ScOH,3H_2O = C_{16}H_{15}O_5Sc,3H_2O.$

Scandium hydroxide is readily attacked by aqueous phenyl-acetic acid, with the formation of a white insoluble phenyl-acetate. The salt thus prepared has, however, a tendency to become more basic, and a better way to prepare it is by double decomposition between ammonium phenyl-acetate and scandium nitrate. When moderately dilute and hot solutions of these salts are mixed and the whole boiled, the phenyl-acetate comes down chiefly on the sides and bottom of the beaker, and adheres to the glass with great pertinacity. It can only be removed with difficulty and risk of breakage. The deposit on the glass looks like warty concretions and under a high power appears crystalline. It is almost insoluble in hot or cold water, and is insoluble in alcohol.

When double decomposition between scandium nitrate and ammonium phenyl-acetate is effected in the cold, the salt comes down as a white curdy precipitate which does not adhere to the glass, and can be washed easily with warm water; boiling water, however, causes it to cohere with contraction. The dry salt when heated softens and can be pressed into a pasty mass. It does not fuse at a temperature at which decomposition begins.

Analysis.

1. 13·584 grs. of scandium phenyl-acetate precipitated from hot solutions and washed with boiling water, filtered, and dried at 100° till the weight was constant, yielded on ignition 2·396 grs. of scandia, = 1·5516 grs. of scandium.
2. 9·458 grs. of scandium phenyl-acetate precipitated from cold solutions, washed, and dried at 100° to a constant weight, gave on ignition 1·671 grs. of scandia, = 1·0821 grs. of scandium.

		Theory.		Experiment.	
				1.	2.
Sc	44·100	11·45		11·42	11·44
C_{16}	192·000				
H_{15}	15·120	341·168	88·55	88·58	88·56
O_5	80·000				
$3H_2O$ ..	54·048				
	385·268	100·00		100·00	100·00

Attempts to estimate the water were unsuccessful, as the phenyl-acetate turned brown and commenced to decompose when heated above 160°, at which temperature the whole of the three molecules of water were not expelled.

Scandium Pyromellitate,

$$C_6H_2\{COOSc(OH)_2\}_4 2H_2O = Sc_4C_{10}H_{10}O_{16},2H_2O.$$

This salt comes down when ammonium pyromellitate is added to a solution of a soluble scandium salt. It is formed also by allowing pyromellitic acid to act on scandium hydroxide with the aid of gentle heat. Scandium pyromellitate is a white amorphous powder, insoluble in water and alcohol, but soluble in dilute acids.

Of the two molecules of water of hydration one is driven off at 100° and the remaining molecule at 140°. The dried salt can be heated to 220° without decomposition.

Analysis.

1. 14·304 grs. of scandium pyromellitate dried at 140° for some hours lost 0·847 gr. of water; when ignited to full redness, treated with nitric acid, and ignited again, it left 6·515 grs. of scandia, = 4·2190 grs. of scandium.
2. 11·485 grs. of scandium pyromellitate dried at 100° lost 0·350 gr. of water, and, when ignited as above, left 5·170 grs. of scandia, = 3·3480 grs. of scandium.
3. 7·614 grs. of scandium pyromellitate heated to 220° for three hours lost 0·464 gr. of water, and, when ignited as already described, left 3·501 grs. of scandia, = 2·2672 grs. of scandium.

		Theory.			Experiment.		
					1.	2.	3.
Sc_4.. ..	176·400	29·47			29·50	29·15	29·78
C_{10}							
H_{10} ..	386·080	64·51			64·58	64·83	64·13
O_{16}							
H_2O ..	18·016	3·01	6·02		5·92	3·05	6·09
H_2O ..	18·016	3·01				2·97	
	598·512	100·00			100·00	100·00	100·00

Scandium Camphorate,

$$C_8H_{14}{<}\begin{matrix}COO\\COO\end{matrix}{>}ScOH.$$

The camphorate is prepared by heating scandium hydroxide with a slight excess of camphoric acid and water. The hydroxide is easily attacked and converted into an insoluble camphorate. It may be prepared also by precipitating a solution of scandium nitrate with a solution of ammonium camphorate. In either case, it forms an insoluble white precipitate, which, after thorough washing and drying at 100°, has the composition given above.

Scandium camphorate is anhydrous and insoluble in water and alcohol. It is easily soluble in dilute mineral acids. When dry it is very electrical, and an attempt to powder it sends it flying out of the mortar. If it is put warm between two watch-glasses, and the lower glass is gently rubbed on the outside with the finger, the path of the finger is marked by a flight of camphorate from the lower to the upper glass, where it sticks. This peculiarity makes it not easy to perform the preliminary operations of drying, transferring, and weighing, preparatory to its quantitative analysis.

Gradually heated to redness, the camphorate at first blackens with carbon. At a red heat this burns off, leaving a white residue of scandia.

Analysis.

1. 18·191 grs. of the camphorate, dried at 100°, yielded on ignition 4·772 grs. of scandia, = 3·0902 grs. of scandium.
2. 17·921 grs. of the camphorate yielded on ignition 4·719 grs. of scandia, = 3·0559 grs. of scandium.

		Theory.		Experiment.	
				1.	2.
Sc ..	44·10	17·01		16·99	17·05
C_{10} ..	120·00				
H_{15} ..	15·12	82·99		83·01	82·95
O_5 ..	80·00				
	259·22	100·00		100·00	100·00

Added April 30th, 1908.

Scandium is remarkable inasmuch as its existence was foretold by Mendeleeff, and called by him ekaboron, eight years before its actual discovery by Nilson. (See D. I. Mendeleeff, "A Natural System of the Elements, and its Application to the Indication of the Properties of Undiscovered Elements," *Russ. Chem. Soc. Journ.*, 1871, iii., pp. 25—56). To-day I may be permitted to indulge still further in speculations on the genesis and degradation of the chemical elements—speculations which a few years ago might have been derided even by a learned Society. But the undoubted fact of the production of helium from radium, the probability that chemical elements of high atomic weight are slowly breaking up into bodies of lower atomic weight, and the suspicion that some well-known chemical elements of low atomic weight are degradation products, embolden me to speculate on the past history and genesis of scandium.

In 1898 I brought before the Royal Society a scheme of the arrangement in Space of the chemical elements in which scandium was seen to fall in place between boron and yttrium. I hesitated to introduce ytterbium into the scheme, as its atomic weight was not known with sufficient accuracy to enable it to be properly placed. To-day it is seen to fill a gap below yttrium, and the group is :—Boron, scandium, yttrium, ytterbium. These four elements have a close relationship, thus :—

B atomic weight	11·0	× 16	= 176·0
Sc „	44·1	× 4	= 176·4
Y „	89·0	× 2	= 178·0
Yb „	173·0	× 1	= 173·0

In reference to this table it must be remarked that the atomic weight of scandium certainly is not known with absolute accuracy, the 0·1 being little more than a guess. Yttrium, moreover, is now seen to be very liable to contain scandium; when Cleve determined its atomic weight it was impossible, without further refined spectroscopic examination—not available at that date—to detect in it the trace of scandium sufficient to lower the atomic weight by one unit. Ytterbium certainly is too low, for Urbain recently has announced the discovery in it of an element of a lower atomic weight; this being removed might raise the atomic

weight of ytterbium a few units. With these reasonable corrections the last column will not be far from the same whole number, 176.

The frequent occurrence of the triad ytterbium, yttrium, and scandium in a very limited group of rare minerals may be explained by assuming the instability of ytterbium, the atom of highest weight, and letting it split into two atoms, when yttrium would be produced. Assume the same action to take place with yttrium, its splitting up again into two atoms would produce scandium; and scandium ("*eka-boron*, next in order to boron") would ultimately form boron by a quadruple sub-division. The comparatively small quantities of ytterbium and scandium in these minerals may easily be accounted for by the assumption that they are more unstable forms of matter than yttrium and boron.

The fact that these bodies give totally distinct line spectra has not the significance it formerly was supposed to have, for now we know of different line spectra given by the same body. Argon, with its red and blue spectra, is a case in point, and Goldstein, as a result of his work on the spectra of Cs, Rb, and K, has come to the conclusion that the property of emitting two separate line spectra is a general one. Moreover, between the line spectra of radium, uranium, and helium—bodies which are supposed to be associated genetically—there is no similarity or line in common.

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W. Crookes. "On Radiant Matter Spectroscopy: Examination of the Residual Glow." *Proc. Roy. Soc.*, February, 1887, vol. xlii., p. 111. "Scandium, either in the form of earth or sulphate, phosphoresces of a very faint blue colour. Addition of lime does not bring out any lines."

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G. Urbain (*Journal de Chimie-Physique*, February, 1906, vol. iv., p. 64) gives a passing reference to scandium as follows:—"In none of my fractions have I been able to observe the presence of scandium. I am led to think that this element does not belong to the group of rare earths, properly so-called. Sir W. Crookes (Chemical News, vol. xci., p. 61) thinks he has detected this element in my gadolinia. [Quite true.—W. C.]. The statement is denied by Eberhard (*Zeit. Anorg. Chemie*, xlv., p. 374)."

THE FORMATION OF GRAPHITE BY THE INTERACTION OF MAGNESIUM POWDER AND CARBONATES.*

By H. RUSSELL ELLIS, B.Sc., F.C.S.

Winkler, in an investigation of the action of magnesium on the carbonates of the alkaline earths, showed that the carbonates were readily reduced on heating, and amorphous carbon was produced in the reaction (*Ber.*, 1890, xxiii., 2642; see also Moissan, "Electric Furnace," p. 38). The properties of this carbon were not investigated by Winkler or by Maquenne, who also studied the reaction between magnesium and the alkaline earth carbonates.

During an investigation of the action of magnesium powder on various carbonates quantities of carbon were produced, and the object of the present paper is to show that this carbon is a mixture of amorphous carbon and graphite; in some cases it consists almost entirely of graphite. The graphite is non-intumescent.

A mixture of a carbonate and magnesium powder does not require heating before action commences. If such a mixture be ignited in one portion by a match or by means of burning magnesium, a reaction similar to Goldschmidt's occurs, and proceeds throughout the whole mass more or less vigorously; in many cases CO is evolved, which causes much of the contents of the crucible to be ejected; if the metal is of comparatively low boiling-point, this distils off and burns, and so renders the reaction more violent. Since this reaction was accompanied by very high temperature, and since at high temperatures graphite is the stable form of carbon, it was thought that the carbon would be present in this form. In all cases this was found to be so, although amorphous carbon was also present, the graphite being formed as such or formed from amorphous carbon at the extremely high temperature of the reaction.

Detection of Graphite in the Reaction Products.

The contents of the crucible, after a reduction had taken place, were boiled for some time with hydrochloric acid, washed, filtered, and dried, and then treated with fuming nitric acid prepared from boiled sulphuric acid, dry potassium nitrate, and dry potassium chlorate. The mixture was kept cold at first, and then placed on a water-bath, and the temperature slowly brought to 100° C., and the solution evaporated to dryness. If the mixture be made at a high temperature, explosion occurs, and at times the whole mass inflames; by mixing in the cold and warming as described above, in no case was any explosion produced. Small quantities only were used; in nearly every case a deep green coloration was produced at the first treatment, and a yellow powder was left after dissolving the humic acids and potassium chloride in the dry residue; if any black powder was left, this was dried and again treated with the oxidising mixture. The complete conversion of the carbon into humic and graphitic acid seldom required more than one treatment. The graphitic acid obtained readily exploded on heating, forming pyrographitic acid.

Estimation of the Amounts of Graphite and Amorpous Carbon in the Mixture.

In Berthelot's memoir on carbon (*Ann. Chim. Phys.*, 1870, Ser. 4, xix., 392), it was shown that fuming nitric acid attacked amorphous carbon, producing humic acids which were soluble in water, and did not attack graphite. This observation has served as the basis of a method of estimating graphite and amorphous carbon in a mixture of the two.

The total ash is estimated in the mixture by ignition in the muffle furnace; the amorphous carbon quickly burns away, whilst the graphite remains for some time, and only slowly burns. Another portion (0·1 to 0·4 grm.) of the mixture is heated on a sand-bath in a conical flask with

* A Paper read before the Faraday Society, December 15, 1908.

fuming nitric acid for several days until no more brown fumes are evolved, fresh additions of nitric acid being added from time to time. After the oxidation is complete the solution is poured out into an evaporating basin, and evaporated to dryness on the water-bath to remove all the nitric acid. The residue, consisting of humic acid, graphite, and insoluble mineral matter, is extracted with water, and filtered through a tared filter-paper, washed, dried, and weighed. It is then finally burnt in the muffle, the loss of which gives the amount of graphite present. It is essential that the nitric acid be removed, as the mixture is difficult to filter and the filter-paper is attacked.

The method was tested by using a mixture of pure graphite (*Trans. Far. Soc.*, Part I., iv., 70) and amorphous carbon, and it was found to give fairly good results, the graphite being 1 to 2 per cent too high, probably owing to the great difficulty of removing traces of moisture.

This method is very tedious and requires much time, so it was not considered worth while to estimate any of the mixtures obtained. Graphite was obtained from the carbonates of the alkaline earths—ammonium carbonate, cadmium carbonate, and magnesium carbonate—and by the action of magnesium on carbon dioxide.

Reduction of Carbonates of Barium, Calcium, and Strontium.

Mixtures were made in the following proportions :—

(*a*) RCO_3+Mg,	(*d*) RCO_3+4Mg,
(*b*) RCO_3+2Mg,	(*e*) $RCO_3+3Mg+2C$,
(*c*) RCO_3+3Mg,	(*f*) $RCO_3+3Mg+6C$,

and the reaction carried out in open crucibles and in closed iron tins at high temperatures.

In all cases the reaction was violent, especially when carbon was initially present, and in all cases graphite was found in the products of the reaction; in the case of reactions (*e*) and (*d*) very little amorphous carbon was produced.

The reaction between barium and strontium carbonates and magnesium powder when carried out in open crucibles always produced the carbide, nitride, and large amounts of cyanide; when the reaction took place in closed tins, the carbides only were produced. With calcium carbonate no carbide, nitride, cyanamide, or cyanide was produced when open crucibles were used; when the reaction took place at high temperatures in closed tins, calcium carbide only was produced. Since results differing from those of Winkler and Maquenne were obtained, a subsequent paper on this subject will be given.

It is well known that most carbides dissolve carbon and deposit them in the form of graphite; that the graphite was not obtained in this way is evident from the fact that the mass had not a fused appearance, but was a very soft powder.

Action of Magnesium on Ammonium Carbonate, Magnesium Carbonate, and Cadmium Carbonate.

The action was vigorous, and produced graphite, but no nitride, cyanide, or carbide.

Action of Magnesium on Carbon Dioxide.

A rapid stream of dry carbon dioxide was passed over 25 grms. of dry magnesium powder, and this was heated strongly at one point.

After a time the magnesium caught fire and burnt rapidly, producing a black and white residue. This powder was treated with hydrochloric acid, and the carbon filtered and dried; about 2·5 grms. were obtained. Only a very slight amount of carbide was formed, no gas being evolved when the powder above was dropped in water; the smell of acetylene, which is very easily observed from minute quantities of the gas, was, however, noticed.

The black powder contained graphite, but only in small quantity.

Percentage of ash	= 6·64
,, graphite	= 12·09
,, amorphous carbon . ..	= 81·27

The reaction in this case is comparatively slow, and the mixture was spread out over a long tube, and consequently no very high temperature was attained; on the other hand, when the reduction takes place in crucibles, the heat is concentrated, and a much higher temperature results, and more of the carbon is changed into graphite.

It seems probable that amorphous carbon is first produced by the action of the magnesium on the carbonate, and that more or less of this is converted into graphite owing to the enormous heat evolved.

COLLOIDAL BARIUM SULPHATE.*

(PRELIMINARY COMMUNICATION).

By ERNEST FEILMANN, Ph.D., F.I.C.

DESCRIPTIONS of the preparation of colloidal barium sulphate are comparatively rare; G. Buchner (*Chem. Zeitung*, 1893, xvii., 878) describes the precipitation of a gelatinous form of this substance on mixing concentrated aqueous solutions of barium acetate and aluminium sulphate, but on dilution or on standing this reverts to the ordinary form. Neuberg and Neumann (*Biochem. Zeit.*, 1906, i., 166) obtain it by the addition of aqueous sulphuric acid to a methyl alcoholic solution of barium hydroxide, as a jelly which forms a porcelain-like mass on ignition. v. Weinarm (*Zeit. Chem. Ind. Kolloide*, 1908, ii., 89) describes the preparation of numerous salts of the alkali earth and alkali metals, including barium sulphate, in the form of jellies. Some years ago the author of the present communication experimented on the protective action of alkali-casein solutions in the production of colloidal solutions of organic and inorganic substances. For various reasons these were not published at the time; the most various substances, including many of the heavy metals and their more insoluble salts, were thus obtained in solutions of great strength and somewhat surprising stability, and it was thought that a description of such a solution and its method of preparation might not be without interest, especially in view of the ready accessibility in large quantities and cheapness of the materials employed.

Twenty-three grms. of commercial casein were dissolved at below 40° C. in water containing 0·09 grm. of sodium hydroxide and diluted to 230 cc. To this solution was added a solution of 14·2 grms. (0·1 mol.) of anhydrous sodium sulphate in water to 200 cc. To this mixed solution a solution of 24·5 grms. (0·1 mol.) of crystallised barium chloride in water to 100 cc. was then slowly added at 20° C. with vigorous stirring. A thick creamy and almost homogeneous liquid was so obtained, though there was a certain amount of sedimentation on standing. It was precipitated by adding 12 cc. of glacial acetic acid, which caused the formation of a white curd-like precipitate, allowed to stand, and the precipitate washed by repeated decantation till free from acid reaction. It was then stirred with 400 cc. of water and 2 cc. of 15 per cent sodium hydroxide solution at 40° C. for three hours, filtered through an open paper filter, and evaporated to dryness on the water-bath. Before evaporation the liquid had much the appearance of ordinary milk by reflected light; by transmitted light it was transparent in thin layers, showing the peculiar reddish yellow tinge so characteristic of many colloidal solutions. The solid obtained by evaporation was translucent, and of a horny appearance and texture. It was quite soluble in water to a similar solution to the one just described, but on standing it appears to undergo some slight change which renders it necessary to employ a very little dilute alkali in order to obtain a perfect colloidal

* A Paper read before the Faraday Society, December 15, 1908.

solution. On ignition 56·7 per cent of barium sulphate were left. After keeping for six months 2 grms. of the substance dissolved in 70 cc. of water and 0·5 cc. of normal sodium hydroxide solution, leaving only a negligible amount of residue. Under a magnification of 200 diameters particles in rapid movement can just be made out under the microscope, and the appearance of the liquid under magnification is much the same as that of the colloidal solutions of tungsten prepared by Kuzel's method. The solutions are very stable; only a slight amount of sedimentation takes place after standing for many hours, and this is very possibly due to the action of the air, which appears in some way to affect the stability of the solution.

The protective action of organic and other colloids in cases such as the one just considered is one that has not yet been adequately explained, though the phenomenon has been known for a very long time. Some light is thrown on this question by the experiments of Michaelis and Pincussohn (*Biologische Zeit.*, ii., 251), who experimented with colloidal suspensions of indophenol and mastix. These were more stable than suspensions of indophenol alone, and microscopic and optical examination of the mixture led to the conclusion that each particle of indophenol was surrounded by a layer of mastix. There is reason to suppose that the colloidal barium sulphate and other preparations of the present author are in a very similar condition, and that each particle of inorganic material is surrounded by a layer of casein; they behave towards acids and alkalis in a very similar manner to casein itself, being precipitated by the former from solution and re-dissolved by the latter, and this process can apparently be carried on alternatively almost *ab libitum*. These facts suggest that the surface in actual contact with the liquid media consists of casein only, and that it is this surface which conditions the stablity of the solutions obtained. This view is also n accordance with the fact that a certain minimum quantity of casein is in each case necessary to hold the inorganic substance in solution.

A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS.*

Part III.—Analysis of the Aluminium and Iron Groups, including Beryllium, Uranium, Vanadium, Titanium, Zirconium, and Thallium.

By ARTHUR A. NOYES, WILLIAM C. BRAY, and ELLWOOD B. SPEAR.

(Concluded from p. 303).

Confirmatory Experiments and References (continued).

Complete Precipitation of Thallium by Ammonium Hydroxide.—20 mgrms. Tl as Tl_2SO_4 were treated with HNO_3 and $HClO_3$ by P. 61, and then with NH_4OH by P. 64; a dark red flocculent precipitate separated. This was filtered off, the filtrate was evaporated nearly to dryness, and tested for thallium with KI by *P. 65*d*; no precipitate of TlI separated, showing that thallium had been completely precipitated by the NH_4OH. Since thallous hydroxide is soluble, it follows also that thallous compounds are completely oxidised by HNO_3 and $HClO_3$ in P. 61.

P. 64, N. 2: *Action of Nitric Acid on Potassium Sulphocyanate.*—In each of a number of test-tubes 1 cc. HNO_3 (1·42) was placed; varying amounts of water (from 0 to 15 cc.) and finally 5 cc. 10 per cent KSCN solution were added; in each case a red colour appeared slowly in the cold, more quickly on warming slightly, and more quickly in the more concentrated HNO_3 solutions. The red solutions were boiled in casseroles; the colour disappeared quickly, and the solutions remained colourless on cooling. More KSCN was added; the colour reappeared uickly. The experiments were repeated with 0·1 mgrm. Fe as $FeCl_3$; a red colour appeared at once in the cold, but on boiling this colour also disappeared in a minute or two. To one of these colourless solutions, after cooling, was added KSCN; the red colour appeared at once. To another was added 0·1 mgrm. Fe as $FeCl_3$; the solution remained nearly colourless. These experiments show that on boiling with HNO_3, the KSCN is completely decomposed, and therefore that the red colour due to nitrous acid cannot be eliminated by boiling.

P. 65, N. 2, 5, *and* 6: *Precipitation of Titanium, Zirconium, and Thallium in the Ammonium Acetate Procedure.*—0·5 mgrm. Ti as $TiCl_4$ in 100 cc. was treated by P. 65; a small precipitate separated, which was proved to contain titanium by *P. 65*b*. The experiment was repeated with 10 and with 500 mgrms. Ti; the filtrates were tested for titanium by evaporating with a little H_2SO_4 to fuming, cooling, and adding H_2O_2; no colour appeared.

A mixture containing 500 mgrms. Fe as $FeCl_3$ and 20 mgrms. Zr as $ZrCl_4$ was treated by P. 65; a large amount of zirconium was found in the precipitate, but on adding NH_4OH to the filtrate a white precipitate was obtained which was estimated to contain 3 to 5 mgrms. Zr. 10 mgrms. Zr as nitrate in HNO_3 solution were treated by P. 65, except that no $FeCl_3$ was added; NH_4OH was added only until a very small precipitate of zirconium hydroxide separated, and the solution was still acid when the ammonium acetate was added; the filtrate from the basic acetate precipitate was made alkaline with NH_4OH to test for zirconium; a white precipitate separated, which was estimated to contain 1 or 2 mgrms. Zr. The experiment was repeated with 1 and 2 mgrms. Zr, except that NH_4OH was added until the solution was neutral; the filtrate was made acid, evaporated to 20 cc., and then made alkaline with NH_4OH; no precipitate separated. The last experiment was repeated with 5 mgrms. Zr as nitrate and 20 mgrms. PO_4 as Na_2HPO_4; no zirconium was found in the filtrate. For the fact that zirconium is not precipitated in the presence of considerable acetic acid, and that it then prevents the complete precipitation of titanium, see Hillebrand (*Bull. U.S. Geol. Survey*, 1900, clxxvi., 72).

20 mgrms. Tl as $TlCl_3$ were treated by P. 65, except that no $FeCl_3$ was added; a brown precipitate separated on boiling and also on adding NH_4OH; the former was two or three times as large as the latter, thus showing that at least 5 mgrms. Tl were not precipitated till the NH_4OH was added. The filtrate was evaporated nearly to dryness; H_2SO_4 was added, and the solution when cold was tested for thallium with KI and Na_2SO_3 by *P. 65*d*; a small precipitate of TlI was obtained which was estimated to contain 0·5 to 1 mgrm. Tl. The experiment was repeated with 1 mgrm. Tl; no precipitate resulted on boiling, nor on adding NH_4OH. The filtrate was proved to contain the thallium. The experiment with 1 mgrm. Tl was repeated, $FeCl_3$ being added as directed in the procedure; no precipitate separated on adding NH_4OH to the filtrate. Both precipitate and filtrate were tested for thallium; about half of the thallium was found in the precipitate and the remainder in the filtrate. The last experiment was repeated with 0·5 mgrm. Tl; a small but distinct test was obtained for thallium both in the precipitate containing the iron and in the filtrate.

*P. 65*a*, N. 1 *to* 3: *Extraction of* $FeCl_3$ *by Ether.*—See Rothe (*Stahl und Eisen*, 1892, xii., 1052; 1893, xiii., 333); Langmuir (*Journ. Am. Chem. Soc.*, 1900, xxii., 102); Kern (*Journ. Am. Chem. Soc.*, 1901, xxiii., 689).

To determine the best concentration of HCl to use in this extraction, a series of experiments was performed as follows:—500 mgrms. Fe as $FeCl_3$ were dissolved in 30 cc. HCl of known specific gravity, and this solution was treated several times with about 35 to 40 cc. ether in a separating funnel as described in the procedure. The amount of $FeCl_3$ extracted in each treatment was estimated by evaporating the ether extract to dryness, adding HCl, and precipitating with NH_4OH. The results are given in the following table. Since the ether used contained initially no HCl, the amount of HCl in the water layer is some-

* From the *Journal of the American Chemical Society*, xxx., No.4.

what decreased in each treatment. The proportion of $FeCl_3$ extracted in each treatment was 4 to 5 per cent with 8 per cent HCl (sp. gr., 1·04); 95 to 96 per cent with 18 per cent HCl (sp. gr., 1·09); 99 per cent with 22 per cent HCl (sp. gr., 1·11); and 94 per cent with 25 per cent HCl (sp. gr., 1·125).

With the 22 per cent acid (sp. gr., 1·11) the first extraction took out nearly all the $FeCl_3$ (495 mgrms. Fe), the second extraction nearly all of 5 mgrms. Fe remaining, and the third only a fraction of a mgrm. A similar result was obtained when 500 mgrms. Fe as $FeCl_3$ were precipitated with NH_4OH, the precipitate dried between filter-papers, and dissolved in HCl (1·12). This result is in agreement with that of Rothe, who recommends an acid of sp. gr. 1·100 to 1·105, for he shook his ether with HCl of this strength before making the separation.

Molecular Formula of Ferric Chloride in Ether Solution.—See Beckmann (*Zeit. Physik. Chem.*, 1903, xlvi., 860).

Extraction of Thallic Chloride by Ether.—15 mgrms. Tl as $Tl(OH)_3$ were treated by *P. 65*a*; the solution of $TlCl_3$ in HCl (1·12) had a yellow colour, but this layer was colourless after it was shaken with ether; the ether layer had a yellowish colour. The first ether extract contained nearly all the thallium, the second ether extract contained less than 1 mgrm., and the water layer after the two extractions was practically free from thallium.

*P. 65*a*. N. 4: *Behaviour of Titanium, Zirconium, and Uranium in the Ether Treatment.*—A solution of 50 mgrms. Ti as $TiCl_4$ in one experiment, and of 50 mgrms. Zr in another, in 30 cc. HCl (1·11) was shaken with an equal volume of ether; the ether layer was evaporated to dryness in a casserole on a water-bath, HCl (1·20) was added and heated, the solution was made alkaline with NH_4OH; no precipitate separated in either case, showing that no titanium or zirconium had dissolved in the ether layer. In the case of titanium the water layer became reddish yellow owing to the presence of H_2O_2 in the ether, and in the case of zirconium a white precipitate ($ZrCl_4$?) separated in the water layer, but when the ether was expelled by evaporation a clear solution resulted. A white precipitate was also found to result with titanium in an experiment in which 300 mgrms. PO_4 were also present.

For proof that uranium is not extracted, see Kern (*Journ. Am. Chem. Soc.*, 1901, xxiii., 689).

*P. 65*a*. N. 5: *Extraction of Iron by Ether in the Presence of Phosphate.*—500 mgrms. Fe as $FeCl_3$ and 300 mgrms. PO_4 as ammonium phosphate were dissolved in 30 cc. HCl (1·09) and treated with ether (35 cc.) as described in the procedure; about 95 per cent of the iron was extracted in each treatment and the phosphate remained in the water layer.

*P. 65*b*, N. 1: *Nature of the Compound of Hydrogen Peroxide with Titanium.*—In regard to the coloured solution and the preparation of solid TiO_3, see Schönn (*Zeit. Analyt. Chem.*, 1870, ix., 41); Classen (*Ber.*, 1888, xxi., 370: Levy (*Ann. Chim. Phys.*, 1892, [6], xxv., 463); Melikoff and Pissarjewsky (*Ber.*, 1898, xxxi., 953).

Mr. Chas. Field, 3rd, working in this laboratory, performed the following migration experiment. A coloured solution was prepared by rotating for three hours pure TiO_3, which had been dried over P_2O_5, with a normal HNO_3 solution which contained 1 mol. H_2O_2 per litre. The resulting solution was 0·087 molal with respect to TiO_3. A large U tube which was partly filled with normal HNO_3 solution was placed in a thermostat at 25°, and the titanium solution was carefully introduced through a tube at the bottom of the U. The surfaces of contact of the two solutions were sharply marked. After a current had passed for eight hours, one of the surfaces of the red solution had moved 4 cm. upward toward the cathode, and the other boundary had moved away from the anode a nearly equal distance. This proves that the colour is due to a cation containing titanium.

Delicacy of the Hydrogen Peroxide Reaction for Titanium.—0·1 mgrm. Ti as chloride was treated by *P. 65*b*; a distinct yellow colour appeared on adding the H_2O_2 solution.

*P. 65*b*, N2: *Precipitation and Separation of Titanium and Zirconium as Phosphate.*—See Hillebrand (*Bull. U.S. Geol. Survey*, 1900, clxxvi., 75).

0·5 and 1 mgrm. Zr and a mixture of 1 mgrm. Zr and 100 mgrms. Ti as chloride were treated by *P. 65*b*; flocculent precipitates formed in every case within ten minutes, but were more distinct after half an hour. 100 mgrms. Ti alone were treated by *P. 65*b*; no precipitate separated in several hours.

10 mgrms. Zr as chloride were treated by *P. 65*b*; the precipitate was filtered off after half an hour, and the filtrate made alkaline with NH_4OH; a small precipitate estimated to contain about 0·3 mgrm. Zr separated. The result was the same when the filtration was made after twenty hours. The experiment was repeated, except that only 3 or 4 cc. phosphate solution were used; the filtrate contained 0·5 to 1·0 mgrm. Zr after half an hour and after one hour. The experiment was repeated, using about 15 cc. phosphate solution; only 0·1 to 0·2 mgrm. Zr remained in the filtrate after two hours.

To a number of solutions, containing 1 mgrm. Zr as chloride and varying amounts of H_2SO_4 (1·20) in 15 cc., were added 5 cc. 7 per cent $Na_2HPO_4.12H_2O$ solution; with 1 and 2 cc. of acid the solutions became turbid at once, and flocculent precipitates settled out within twenty minutes; with 5 cc. acid the solution remained clear for about ten minutes, but after one hour there was a distinct precipitate; with 10 cc. acid the solution remained clear for a longer time and only a minute precipitate separated in 1·5 hours.

Precipitation of Titanium with Zirconium Phosphate.—10 mgrms. Zr and 10 mgrms. Ti as chlorides were treated by *P. 65*b*; the precipitate when collected on a filter was distinctly yellow, and this colour remained after washing with water for an hour. About 10 cc. 15 per cent HF solution were poured through the filter in a celluloid funnel and the solution was treated again by *P. 65*b*; the phosphate precipitate was white, and the titanium in the solution was estimated from the colour to be about 1 mgrm. 0·1 mgrm. Ti and 100 mgrms. Zr as chlorides were treated by *P. 65*b*; the solution became distinctly yellow on adding H_2O_2, and the filtrate from the phosphate precipitate was also yellow, showing that titanium is not completely carried down by the zirconium. (100 mgrms. Zr alone gave no colour with H_2O_2).

*P. 65*b*, N. 3: *Precipitation of Thorium as Phosphate.*—2, 5, and 50 mgrms. Th as nitrate were treated by *P. 65*b*; white gelatinous precipitates separated on the addition of Na_2HPO_4, the precipitate being small and forming slowly in the experiment with 2 mgrms. Th. In the experiment with 5 mgrms. a 10 cc. portion of HF (1 volume 45 per cent HF to 2 volumes water) was poured several times through the filter; the solution was evaporated with H_2SO_4 to fuming, cooled, diluted, and excess NH_4OH added; no precipitate separated at once, and only a very small one on standing an hour.

*P. 65*b*, N. 4: *Behaviour of Manganese, Cobalt, Uranyl, and Vanadyl Salts in the Tests for Titanium and Zirconium.*—100 mgrms. Mn as $MnCl_2$ were treated by *P. 65*b—c*; with H_2O_2 no colour resulted, and no precipitate formed when Na_2HPO_4 was added, nor on standing one hour. After the addition of just sufficient powdered Na_2SO_3 to reduce the H_2O_2 (determined by testing portions of the solution with Ti solution), no precipitate formed, but when about 1 grm. more Na_2SO_3 was added a large precipitate separated. The experiment was repeated separately with 100 mgrms. Co as $CoCl_2$ and with 5 mgrms. U as $UO_2(NO_3)_2$; there was no change of colour with H_2O_2 and no precipitate with Na_2HPO_4 on adding enough Na_2SO_3 to destroy the H_2O_2. The experiment was repeated with 100 mgrms. U as $UO_2(NO_3)_2$; the solution was distinctly yellow before the H_2O_2 was added, and a large white precipitate formed on adding just sufficient Na_2SO_3 to decompose the H_2O_2.

10 and 100 mgrms. V as Na_3VO_4 were treated in separate experiments by *P. 65*b*—*c*; with the 10 mgrms. the colour obtained on adding H_2O_2 was similar to that obtained with 3 to 5 mgrms. Ti; with the 100 mgrms., however, the colour was of a much redder shade than that with titanium; on the addition of an excess of Na_2SO_3 the colour changed at once to blue, showing the presence of a vanadyl salt, and no precipitate had separated in either case after several hours in the cold or on boiling.

*P. 65*c*, N. 1: *Behaviour of Titanium in Acid Solutions towards Sodium Phosphate.*—To a solution containing 0·5 mgrm. Ti as chloride and 2 cc. H_2SO_4 (1·20) in 10 cc. were added 10 cc. 7 per cent $Na_2HPO_4 \cdot 12H_2O$ solution; the solution remained clear for ten minutes, but had become distinctly turbid in half an hour. Several solutions, containing 10 mgrms. Ti as chloride and varying amounts of H_2SO_4 (1·20) were treated in the same way; the flocculent precipitates were filtered off after ten minutes, and the filtrates were made alkaline with NH_4OH; in the experiment with 2 cc. acid the filtrate contained 0·5 to 0·1 mgrm. Ti; in that with 3 cc. acid, 1 to 3 mgrms. Ti; in the experiment with 5 cc. acid 3 to 4 mgrms. Ti.

10 mgrms. Ti as chloride were treated by *P. 65*b*—*c*, and after half an hour the mixture was filtered, and the filtrate made alkaline with NH_4OH; a very small precipitate was obtained containing about 0·5 mgrm. Ti. The experiment was repeated with 0·5 mgrm. Ti; the solution became distinctly turbid on decolorising with H_2SO_3. Half of the turbid solution was heated to boiling; a distinct, flocculent precipitate was obtained. The other half was allowed to stand in the cold for half an hour; the precipitate in this case also became somewhat flocculent.

*P. 65*d*, N.: *Test for Thallium with* KI.—0·5, 0·2, and 0·1 mgrm. Tl as Tl_2SO_4 were treated by *P. 65*d*, the total volume being about 10 cc.; a distinct yellow finely divided precipitate of TlI was obtained in each experiment, even in that with 0·1 mgrm. Tl. For proof that 500 mgrms. ferric iron does not interfere with the test, see T. A., No. 174—6.

*P. 65*d*, N. 3: *Flame Test for Thallium.*—0·5, 0·2, and 0·1 mgrm. Tl were precipitated by *P. 65*d* as TlI. The precipitates were collected on small filters and washed twice with a very little water. The moist filter was removed from the funnel, a looped platinum wire was drawn across its surface to collect a little of the precipitate, and introduced into a colourless gas flame; with 0·5 mgrm. Tl the momentary green colour was generally seen, but it was sometimes obscured by the yellow flame, due to sodium and to small fibres of paper; with 0·2 and 0·1 mgrm. Tl the green colour could not be detected with certainty. The experiments were repeated, except that the TlI precipitates were collected on hardened filters; the green flame was much more brilliant with 0·5 and 0·2 mgrm. Tl than in the corresponding experiments with ordinary filter-paper; it could, however, scarcely be seen with 0·1 mgrm. Tl.

P. 69, N. 1: *Potassium Cobaltic Nitrite.*—See Fisher (*Pogg. Ann.*, 1848, lxxiv., 115; Sadtler (*Am. Journ. Sci.*, 1870, [2], xlix., 196); Rosenheim and Koppel (*Zeit. Anorg. Chem.*, 1898, xvii., 35).

P. 69, N. 2: *Precipitation of Cobalt with Potassium Nitrite.*—0·1 and 0·3 mgrm. Co as $CoCl_2$ were treated by P. 69; in each experiment the solution became distinctly turbid within five minutes. The experiment was repeated in the absence of cobalt; the solution remained perfectly clear. For the detection of 0·5 mgrm. Co in the presence of 250 mgrms. Ni in P. 69, see T. A., 127.

500 mgrms. Co as nitrate were treated by P. 69; the mixture was shaken well, allowed to stand, and filtered after about half an hour, and again allowed to stand; a considerable precipitate again separated. The experiment was repeated except that the mixture was heated on a water-bath to 50 or 60° with frequent shaking for half an hour; it was allowed to cool, and filtered; no precipitate separated in the filtrate even on standing over night.

Separation of Nickel from Cobalt with Potassium Nitrite.—500 mgrms. Co and about 5 mgrms. Ni as nitrates were treated by P. 69; after standing twenty hours the mixture was filtered; the filtrate was evaporated almost to dryness with HCl, and made alkaline with NaOH; only a very small green precipitate separated corresponding to not more than 2 mgrms. Ni. Half of the cobalt precipitate obtained was treated by P. 70; a very good test for nickel was obtained. The experiment was repeated except that the mixture was heated on a water-bath for half an hour; less nickel was found in the filtrate than in the preceding experiment.

Precipitation of Potassium Nickelous Nitrite. — 250 mgrms. Ni (previously freed from cobalt by a KNO_2 treatment) were treated by P. 69, except that the volume was cut down to 50 cc. without, however, altering the total amount of reagents used; a distinct reddish coloured precipitate separated within twenty minutes which was proved to contain nickel but no cobalt by the borax bead test. For the action of HNO_2 on nickel salts and the formation of $K_4Ni(NO_2)6$, see Lang (*Journ. Prakt. Chem.*, 1862, lxxxvi., 299); Hampe (*Lieb. Ann.*, 1863, cxxv., 346); and Reichard (*Chem. Zeitung.*, 1904, xxviii., 479, 885, 912).

P. 70, N. 2: *Delicacy of Hypobromite Test for Nickel.*—150 mgrms. Co free from nickel were treated by P. 70; no precipitate was observed, not even on filtering. The experiment was repeated except that 0·15 mgrm. Ni as $NiCl_2$ was added; the solution became dark coloured on adding excess NaBrO, but no precipitate collected; it was easily seen, however, on the filter. 0·2 mgrm. Ni as $NiCl_2$ was treated by P. 70; a distinct precipitate was obtained on filtering.

Separation of Nickel from Cobalt by Hypobromite.—200 mgrms. Co and 0·5 mgrm. Ni as chlorides were treated by P. 70; the precipitate was tested for cobalt in the borax bead; no blue colour was obtained.

A large number of experiments were performed to determine the proper conditions for making this separation. In working with cobalt free from nickel, it was found that a precipitate of $Co(OH)_3$ always formed when the NaBrO reagent (or bromine water and NaOH) was added very soon after the addition of KCN, and that the necessary interval of time was greatly shortened by increasing the excess of KCN added.

The following experiments show that excess of NaBrO is essential to the precipitation of nickel. 1 mgrm. Ni as $Ni(NO_3)_2$ was treated by P. 69; the NaBrO solution was added in small portions, and after the addition of each portion the solution was tested with the starch KI paper; as long as this paper remained colourless no precipitate of $Ni(OH)_3$ separated, but after the precipitate formed the paper became blue when dipped into the mixture. The experiment was repeated with 10 mgrms. Ni. As long as the precipitation was incomplete the paper remained colourless, or only a small brown ring was formed on the paper, but after complete precipitation all of the paper immersed in the solution became brown or blue.

P. 70, N. 4: *Action of* H_2S *on Alkaline Tartrate Solutions containing Nikel or Cobalt.* — Villiers (*Comptes Rendus*, 1894, cxix., 1263; 1895, cxx., 46) found that when H_2S was passed into a NaOH containing freshly precipitated $Ni(OH)_2$ (but no tartrate) the hydroxide was quickly converted into black nickel sulphide, but that a portion of the nickel passed into solution giving a deep brown colour, proving that the presence of tartrate is not essential for the formation of the brown solution. 0·5 mgrm. Ni as nitrate was treated by both parts of P. 70; a deep brown solution was obtained on saturating the alkaline tartrate solution in a test-tube with H_2S. 0·1 and 0·2 mgrm. Ni as nitrate were dissolved in a little HNO_3 and treated by the second paragraph of P. 70, about 5 cc. of 10 per cent tartaric acid and 5 cc. excess of NaOH being added; clear dark yellow solutions were obtained on saturating with H_2S. The experiment was repeated with 1 mgrm. Ni; on passing in H_2S the solution remained nearly colourless for about one

minute, but finally a clear dark brown solution resulted. The experiment was repeated with 20 mgrms. Ni; on saturating with H_2S the liquid in the test-tube was opaque and almost black in colour. The liquid was filtered; very little precipitate remained on the filter. It was allowed to stand several hours; a black precipitate separated but the filtrate was still black and opaque.

20 mgrms. Co as $CoCl_2$ in a little dilute HNO_3 were treated by the second paragraph of P. 70; a black precipitate separated as soon as the H_2S was led in and the cobalt was completely precipitated within one minute. The mixture was filtered, the filtrate was saturated with H_2S, and the test-tube corked and set aside; the solution remained colourless for several hours. A similar solution was exposed to the action of the air in an open flask; it became dark yellow in about one hour owing to oxidation of the sulphide and consequent formation of polysulphide. The experiment was repeated except that 1 mgrm. Ni as $NiNO_2$ was also present; the excess of 10 per cent NaOH was 4 or 5 cc.; H_2S was led into the solution for about one minute and the CoS filtered off; the nitrate was nearly colourless. This was saturated with H_2S; it became brown, the colour being such as to indicate that very little of the nickel had been carried down with the cobalt. This experiment was repeated except that the H_2S was led through the solution for five minutes before the CoS was filtered off; the filtrate was of a lighter brown than before, indicating that over half the nickel had been carried down with the cobalt. The experiment was repeated except that the CoS was not filtered off till after ten minutes; the filtrate was almost colourless, and remained so on saturating again with H_2S. The experiment was repeated, the CoS being filtered off after half an hour; the filtrate was colourless and contained no nickel. In a similar series of experiments in which a smaller excess of NaOH than 4 to 5 cc. was added, the filtrate was light brown after one minute, and nearly colourless after five minutes, thus showing that there is more danger of losing nickel when the excess of alkali is small, in which case the brown solution is formed more quickly. This result that NiS is deposited on CoS after the separation of the latter was confirmed by several experiments.

Similar experiments were made with a mixture of 20 mgrms. Fe as $FeCl_3$ and 1 mgrm. Ni, and with one of 20 mgrms. Mn and 1 mgrm. Ni; good tests for nickel were obtained in both cases.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 3rd, 1908.

Sir WILLIAM RAMSAY, K.C.B., F.R.S., President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Herbert Edwin Cocksedge, B.A., 5, Romola Road, Herne Hill, S.E.; Frederick Percy Dunn, B.Sc., Haresfield. Chorley Wood; Frederic Ferraboschi, B.A., Clare College, Cambridge; Walter Norman Haworth, M.Sc., Dacca House, Chorley; Eric Hayward, care of W. R. Criper, Esq., Konnager House, Konnager, near Calcutta; Robert Ernest Jackson, York Villa, Shepherd's Lane, Dartford; John Hugh Jeffery, 10, Daysbrook Road, Streatham Hill, S.W.; Joseph Allen Pickard, B.Sc., 3, West Kensington Terrace, W.; David Segaller, 69, Dover Road, Wanstead Park, E.; Reginald Wells Varley, 12, Mill Hill Road, Derby.

A ballot for the election of Fellows was held, and the following were declared duly elected:—Noel Charles Akers; Thomas Boles Allen, M.A.; Thomas Aubertin, B.A.; Maung Ba, B.A.; Thomas James Baker, D.Sc.; Maurice Barrett; Prince Mom Chow Bhunsri; Robert Bickerstaffe; William Colet Birch, B.A.; William Sudderick Brakes; Leonard Clement, B.A.; Robert Charles Cowley; Hugh Cecil Duckworth; Horace Barratt Dunnicliff, B.A., B.Sc.; Reginald Freeman Easton; Charles Everitt, M.A.; Henry Fairburn; Arthur Frank Girvan, B.Sc.; Henry Hamilton Green; John Griffin, B.A.; John Henry Albert Hebron, B.Sc.; Edward Hinks, B.Sc.; Joseph Albert Hughes; Thomas Ernest Hull; James Colquhoun Irvine, D.Sc., Ph.D; Grove Johnson; Patrick Anderson Keiller, B.Sc.; Joseph Kenyon, B.Sc.; H. V. Krishnayya, B.A.; Frank William Linch; Arthur Stanley Lindley; Gregor MacGregor, M.A., B.Sc.; Frederick Martin Kay Menzies, M.D., F.R.C.P.; William Herbert Miles; Charles James Millar; Edward Pigott Minett, M.D., M.R.C.S., L.R.C.P.; Howard Houlston Morgan, B.Sc.; Cyril Lawrence Norman; Alexander Robert Normand, M.A., B.Sc.; George Edward Pearson; John William Pearson, B.A.; Frank Perry; George O'Brien Power; Alexander Rennie; Ezra Lobb Rhead; William Frothingham Roach, M.D.; Maurice Salomon Salomon; Maung U. San; William Saunderson, B.Sc.; Herbert M. Shilstone, B.Sc.; Ernst Sommerfeldt, Ph.D.; Francis George Henry Tate; Frank Moreton Thomas; Sidney Gilbert Walton; John Watt, M.A.; Robert Dickie Watt, M.A., B.Sc.; Arthur Weighell; Frederick Williams, B.A.; William George Winterson, B.Sc.; William Ord Wootton, B.Sc.; Frederick Palliser Worley, M.A., M.Sc.; Allister McLean Wright.

Of the following papers, those marked * were read:—

*251. *Double Salts of Potassium Iodide with Mercuric Iodide and Dimercuriodocamphor in Organic Solvents.*" By JAMES ERNEST MARSH and ROBERT DE JERSEY FLEMING STRUTHERS.

When an aqueous solution of compound K_2HgI_4 is shaken with ether, ethyl formate, or some other organic solvents, the salt, $KHgI_3$, is extracted; it separates from its solution in ethyl formate as a heavy oil. In no case was the original salt, K_2HgI_4, dissolved. With camphor, the *double* salt, $KHgI_3.4C_{10}H_{16}O$, was obtained from dilute alcohol in light yellow gritty crystals melting at 65°.

Potassium iodide and dimercuriodocamphor, $C_{10}H_{14}OHg_2I_2$, also form a *double* salt readily soluble in acetone or alcohol, although the two constituents are separately very sparingly soluble.

*252. "*The Action of Mercuric Iodide on Ketones in Alkaline Solution.*" By JAMES ERNEST MARSH and ROBERT DE JERSEY FLEMING STRUTHERS.

Acetone reacts with mercuric iodide in cold aqueous potassium hydroxide according to the equation:—

$$C_3H_6O + 8HgI_2 + 6KHO = C_3OHg_5I_4 + 3K_2HgI_4 + 6H_2O.$$

Diethyl ketone reacts mainly according to the following equation:—

$$(C_2H_5)_2CO + 6HgI_2 + 4KHO = (CH_3{\cdot}CHg_2I_2)_2CO + 2K_2HgI_4 + 4H_2O.$$

Acetophenone reacts as follows:—

$$C_6H_5{\cdot}CO{\cdot}CH_3 + 6HgI_2 + 4KHO = HgI,C_6H_5{\cdot}CO{\cdot}CHg_3I_3 + 2K_2HgI_4 + 4H_2O.$$

The ketone mercury compounds form yellow precipitates. Both the yield and the composition of the precipitates agree with the equations given. In the case of acetone and diethyl ketone, standard alkali was used, and the amount converted into potassium iodide was determined. This amount also agrees with the above equations. The reaction thus affords a quantitative method for estimating the amount of ketones, either by weighing the precipitate formed, or by determining volumetrically the amount of alkali neutralised in the reaction.

*253. "*The Condensation of Camphor with Mercuric Iodide.*" By JAMES ERNEST MARSH and ROBERT DE JERSEY FLEMING STRUTHERS.

The following series of mercury camphor derivatives has been obtained:—

(A) $(C_{10}H_{15}OHg)_2O$, and its salts; (B) $C_{10}H_{14}OHg_2I_2$; (C) $(C_{10}H_{14}O)_2Hg_3O$; (D) $(C_{10}H_{14}O)_3Hg_4I_2$; (E) $(C_{10}H_{14}O)_4Hg_5I_2$; (F) $(C_{10}H_{14}O)_5Hg_6I_2$.

Of these compounds, B, D, E, and F are formed directly by the action of mercuric iodide on camphor in the presence of alkali. B is formed by the action of potassium ethoxide in alcoholic solution on camphor and mercuric iodide in the cold.

D is formed in a hot aqueous solution of potassium hydroxide containing excess of potassium iodide.

E is formed in a similar way with just sufficient potassium iodide to retain the mercuric iodide in solution.

F is formed when there is a defect of potassium iodide.

B is formed from D or E by the prolonged action of hot potassium hydroxide until all the iodine is removed.

Glacial acetic acid converts D into the *compound*, $C_{10}H_{14}OHg_2I_2$, which is insoluble, and the acetate of mercury camphor, which dissolves. From the latter, the base A is separated by the action of sodium hydroxide. The base forms salts, of which the *benzoate*, *sulphate*, *chloride*, *bromide*, and *iodide* have been prepared.

Discussion.

Dr. M. O. Forster inquired whether definite products had been obtained by the dry distillation of these derivatives of camphor, some of which might be expected to yield dehydrocamphor; also whether any therapeutic value had been observed in connection with them.

Mr. Marsh replied that the compound $C_{10}H_{14}OHg_2I_2$ could be sublimed without decomposition, and that the other compounds decomposed, but the products formed had not been examined.

The material used in the experiments was the ordinary dextrorotatary camphor; the therapeutic and physiological action of the compounds had not yet been investigated.

*254. "*The Relation between Absorption Spectra and Chemical Constitution.* Part XIII. *Some Pyrones and Allied Compounds.*" By Edward Charles Cyril Baly, John Norman Collie, and Herbert Edmeston Watson.

The absorption spectra of dimethylpyrone, chelidonic acid, xanthochelidonate, ethyl diacetylacetone, and several other substances have been examined in considerable detail. In many cases the spectra vary with the solvent used, and consequently it seems probable that these compounds can exist in more than one form. Diacetylacetone in particular may be either an open-chain compound or one with a ring formation.

The pyrones and their simpler derivatives appear to contain an oxygen bridge, the atom of oxygen in the ring being quadrivalent. This bridge is broken by the addition of a sufficient quantity of alkali, intermediate compounds being sometimes formed.

*255. "*Organic Derivatives of Arsenic.* Part I. *Dicamphorylarsinic Acid.*" By Gilbert T. Morgan and Frances M. G. Micklethwait.

Dicamphorylarsinic acid, $HO{\cdot}OAs(C_{10}H_{15}O)_2$, colourless prismatic crystals, m. p. 266°, $[\alpha]_D$ 186·6°, is precipitated by acids from an alkaline extract of the product of the interaction of arsenious chloride and sodium camphor in toluene. Its *silver* salt, $AgO{\cdot}OAs(C_{10}H_{15}O)_2$, is a white, sparingly soluble substance, whereas its alkali salts dissolve readily either in water or alcohol. The acid is hydrolysed into camphor (2 mols.) and alkali arsenate (1 mol.), but only when its solution in aqueous caustic alkalis is evaporated almost to dryness.

When treated with phosphorus pentachloride, the acid gives rise to a *chloride*, from which the *anilide* may be obtained.

The authors are engaged in a study of the reactions occurring between the chlorides of the non-metals and organic compounds containing the characteristic group $CH_2{\cdot}CO$.

Discussion.

Dr. Lowry said he had gathered from the title that the compounds to be described were derivatives of camphoric acid. The use of the term "camphoryl" in this sense had been rendered inevitable by the analogy of "acetyl," "benzoyl," "carbonyl," &c., and had been so generally recognised that no alternative name had hitherto been suggested. The use of the same term for the camphor radicle $C_{10}H_{15}O$ was bound to lead to confusion, and it was very desirable that some distinguishing name should be adopted for this group. Camphor derivatives had usually been named by means of prefixes, but the case of "camphocarboxylic acid" suggested an alternative usage: could not the arsenic compound be described by an analogous name as "dicamphoarsenic acid"?

Dr. M. O. Forster defended the use of the expression "camphoryl" for the complex $C_{10}H_{15}O$, and invited Dr. Lowry to formulate "dicamphorylarsinic acid" on his assumption that camphoryl should stand for the radicle of camphoric acid.

In reply to Dr. Pyman, Dr. Morgan said that they had not hitherto obtained the corresponding arsonic acid from the products of this condensation. With reference to the question of nomenclature raised by Dr. Lowry, it seemed to the authors that the prefix "camphoryl" was a suitable one to use for this acid, in which opinion they had the support of other investigators of camphor derivatives.

*256. "*Tellurium Dicyanide.*" By Herbert Edwin Cocksedge.

When tellurium tetrabromide and silver cyanide are heated together for some days in boiling benzene, tellurium dicyanide is formed.

On extracting the residual silver salts with ether, and evaporating the ether at the ordinary temperature, white crystals of the composition $2Te(CN)_2,(C_2H_5)_2O$ are obtained. By heating these and subliming the product in a vacuum, the pure *dicyanide*, $Te(CN)_2$, results in the form of white crystals.

The compound is partly decomposed by heat, giving cyanogen and tellurium. It is at once hydrolysed by water, with precipitation of black flocks of tellurium.

*257. "*Boron Thiocyanate.*" By Herbert Edwin Cocksedge.

Boron thiocyanate, $B(SCN)_3$, is prepared by the action of boron bromide on silver thiocyanate in cold benzene solution. On evaporation of the solvent at the ordinary temperature, colourless crystals remain.

The compound resembles the corresponding thiocyanates of phosphorus and silicon in general reactions, but decomposes readily on heating. The action of aniline on the compound in benzene solution points to the thiocyanate constitution.

*258. "*The Viscosity of Fuming Sulphuric Acid.*" By Albert Ernest Dunstan and Robert William Wilson.

The authors have investigated the viscosity-concentration curve afforded by various mixtures of sulphuric acid and sulphur trioxide. They find a maximum point at the concentration corresponding with H_2SO_4,SO_3.

Discussion.

Dr. Senter said that the maxima in the curves for binary mixtures obtained by plotting viscosity against composition were usually somewhat difficult to interpret. Both sulphuric acid and water appeared to exist as very complex molecules in the pure state, and it was probable that both of them were in a simpler molecular condition when mixed. He wished to ask Mr. Dunstan how, in his opinion, the viscosity curve would be affected by a progressive simplification of the molecules of the components on dilution. If it was assumed that, owing to the increased surface of the particles, the effect of this simplification was to increase the viscosity, the maximum in certain binary mixtures of associated liquids (for example, alcohol and water) could be accounted for without assuming that the components enter into chemical combination. On the other hand, independent evidence pointed to the existence of chemical compounds in mixtures of sulphuric acid and water, and the latter system was therefore very complicated.

Mr. Dunstan, in reply to the President, agreed as to the advisability of determining the molecular surface energy of the mixture, the composition of which approximated to H_2SO_4,SO_3; in answer to Dr. Senter, he said that there were two explanations to the maximum points in viscosity-concentration curves; Jones and Veazey (*Am. Chem. Journ.*, 1907, xxxvii., 405) have asserted that such maxima are due to dissociation; that is, by the proportionally larger frictional surfaces of smaller molecular masses, but he himself contended that in the first place the maxima correspond with aggregates of simpler molecular composition, that such aggregates have actually been isolated, and that heat effects and many other physical properties attain their maxima at the same points. The argument as to larger frictional surfaces only held good if it were definitely known that the aggregates are regular in shape and smooth in surface.

Moreover, since associated substances were proportionately more viscous than non-associated compounds, he considered that the action of the sulphuric acid on the water (and *vice versâ*) was (1) simplification of the homogeneous aggregates, and then (2) association of these products.

259. "*The Decomposition of Carbon Dioxide by the Silent Electric Discharge.*" By Alfred Holt, jun.

Carbon dioxide, which had been carefully dried by phosphoric oxide, was found to be decomposed to an amount which increased as the pressure of the gas diminished. About 48 per cent decomposition was obtained under 30 mm. pressure, and about 3 per cent decomposition under 700 mm. pressure.

The amount of decomposition was found to vary with the degree of dryness of the gas, the intensity of the discharge, and the form of ozoniser employed, but in all cases diminished pressure gave greater decomposition.

Moist carbon dioxide was found to decompose to a larger extent as the pressure of the gas increased, ranging from 3 per cent decomposition under 50 mm. pressure to about 14 per cent under 700 mm. pressure. The weaker the discharge the less gas was decomposed at all pressures.

Comparison of these results with those obtained when moist and dry carbon dioxide is decomposed by ultra-violet light, or induction sparks, leads to the conclusion that the silent discharge at low pressures acts chemically, mainly like ultra-violet light, whilst as the pressure of the gas increases, it behaves more and more as though it consisted of actual sparks.

260. "*Note on Oxalyl Chloride.*" By Humphrey Owen Jones and Hubert Sanderson Tasker.

The authors' investigations on the properties and reactions of oxalyl chloride had been in progress some months when a paper on the same subject was published by Staudinger (*Ber.*, 1908, xli., 3558). It was found, in agreement with Staudinger, that the yield of oxalyl chloride obtained by Fauconnier's method, namely, by the action of phosphorus pentachloride on ethyl oxalate, is very poor, but the yield can be enormously increased by carrying out the reaction at 160° under pressure.

It was found impossible to free the oxalyl chloride entirely from phosphorus compounds by distillation, as the process is rendered more difficult by the presence of *as*-dichloroethane among the products. The amount of phosphorus trichloride formed is small, and the chief product is phosphoryl chloride; ethyl chloro-oxalate and ethyl trichloroacetate are formed in large quantities.

The major portion of the oxalyl chloride distils at about 70°, and then contains about 3 per cent of phosphoryl chloride. Oxalyl chloride reacts vigorously with water, and yields some oxalic acid, together with carbon monoxide and carbon dioxide, whereas Staudinger states that oxalic acid is only obtained when the vapours react.

Oxalyl chloride reacts vigorously with primary and secondary amines to produce substituted oxamides, whereas with tertiary amines it forms additive products. The *additive* compound with pyridine, $C_2O_2Cl_2,2C_5H_5N$, is a white solid, which reacts with water to give pyridine hydrochloride with carbon monoxide and dioxide, and no oxalic acid; it reacts with primary or secondary bases to give pyridine hydrochloride and substituted oxanilides. This is a better method of preparing these substances than by using the chloride direct. The compounds formed with tertiary amines resemble closely the corresponding compounds obtained from carbonyl chloride.

The authors are at present engaged in examining the reactions of oxalyl chloride on a number of substances, chiefly derivatives of organic metallic compounds.

261. "*The Densities of Krypton and Xenon.*" By Richard B. Moore.

The author has prepared pure xenon and krypton from the residues from 120 tons of liquid air. The density of xenon was found to be 65·35, and that of krypton 41·506, the atomic weights being, on the assumption that the gases are monatomic, 83·012 and 130·70 respectively (O = 16).

262. "*The Action of Reducing Agents on Tannic and Gallic Acids.*" By Walter Myers Gardner and Herbert Henry Hodgson.

The object of the work was to devise a rapid and accurate method for the estimation of tannic and gallic acids, and it was thought that a quantitative yield of benzoic acid might be obtained on reduction. Previous work on the action of reducing agents on these acids had been published by Böttinger (*Annalen*, 1890, cclviii., 252) and Guignet (*Comptes Rendus*, 1891, cxiii., 200). The former obtained no reduction products, but using different conditions Guignet found that both tannic and gallic acids were converted into benzoic acids.

The authors have repeated Guignet's work, but obtained a very poor yield of benzoic acid. In the further work, the following were tried as reducing agents:—Zinc, sodium, magnesium, aluminium, sodium hyposulphite, and hydriodic acid; experiments being made in most cases under acid, alkaline, and neutral conditions. The general results were that tannic and gallic acids are little affected by neutral or acid reducing agents, but that they react readily in alkaline solution. In no case, however, was a quantitative yield of benzoic acid obtained, and this was shown to be due to the slow destruction of benzoic acid by alkaline reducing agents.

The original object of the investigation was therefore not attained, but several interesting observations were made.

263. "*The Action of Iodine on Phenols and a Modified Process for the Estimation of Tannic Acid.*" By Walter Myers Gardner and Herbert Henry Hodgson.

In the preceding paper, the authors have shown that tannic acid in alkaline solution rapidly reacts with reducing agents, and, based on this observation, a quick and accurate method for the estimation of tannic acid has been developed. The process is carried out as follows:—To an aqueous solution of tannic acid, standard iodine solution is added in excess. Aqueous sodium hydroxide is then added drop by drop until the colour due to the iodine disappears, after which concentrated hydrochloric acid is added in sufficient excess to precipitate the unabsorbed iodine, the amount of which is estimated by standard sodium thiosulphate. Two estimations are necessary in the case of commercial tannins. Firstly, that of the total iodine absorbed, and secondly, that of the iodine absorbed after removing the tannic acid from the solution by precipitation with gelatin; the difference giving the iodine absorbed by the tannic acid. Previous work by Messenger and Nortmann (*Ber.*, 1890, xxiii., 2753), F. Musset (Chemical News, 1885, li., 42), and A. Moullade (*Journ. Pharm. Chim.*, 1905, xxii., 153) on somewhat similar lines has been repeated, and it has been further shown that the process is available for the estimation of many phenols; for example, phenol, catechol, quinol, salicylic acid, pyrogallic acid, and gallic acid, in addition to tannic acid. With these substances, the amount of iodine absorbed is in direct ratio to the number of hydroxyl groups present, one

hydroxyl group requiring one molecule of iodine ; but with other phenols the reaction, although quantitative, is empirical. The presence of other groups, such as NO_2, NH_2, OMe, as well as the position of the hydroxyl groups in the benzene nucleus, was found to have a determining influence on the course of the reaction. Following Wijs's investigations on the action of Hübl's solution, the authors think that the active substance is the hypoiodate formed, but they are further investigating this assumption.

264. "*Ester Catalysis and a Modification of the Theory of Acids.*" By Edward Fitzgerald and Arthur Lapworth.

The previous observations on esterification and ester hydrolysis in acetone already referred to (*Proc.*, 1908, xxiv., 152) have been confirmed and extended.

If it be assumed that hydrogen ions are responsible for acid catalysis in esterification and ester hydrolysis, the authors find it possible to explain the facts on one proposition only, namely, that the addition of water to a solution of an acid in acetone or alcohol greatly diminishes the number of hydrogen ions, the alternative theories—that the intermediate products are shared between the alcohol and water, or the view applied by Arrhenius to the hydrolysis of salts of weak bases—having proved inadequate.

It would then appear that the proportion of hydrogen ions in an aqueous solution of hydrogen chloride must be extremely small, and this makes it seem probable that they are not altogether indispensable to a satisfactory theory of acids.

The hydrated hydrogen ion or hydroxonium ion, H_2O, often assumed to be the conducting positive ion in aqueous solution of acids, is, in this conception, inert as a catalyst, so that these suggestions are not only at variance with the Arrhenius-Ostwald view of connection between conductivity and reactivity, but are essentially opposed to theories of hydrion catalysis in which the hydroxonium ion is regarded as catalytically active (compare Goldschmidt and Udby, *Zeit. Physik. Chem.*, 1907, lx., 731).

In most physical measurements the hydrogen ions proper may be neglected, and the above theory virtually takes the form that the anticatalytic effect of water on catalysis by acids is due to the fact that water in the same sense as ammonia is a more powerful base than the solvent, and, usually, the substance catalysed, and diminishes the available free acid by converting it into hydroxonium salt.

265. "*An Examination of the Conception of Hydrogen Ions in Catalysis, Salt Formation, and Electrolytic Conduction.*" By Arthur Lapworth.

Small quantities of water depress the catalytic effect of acids on the bromination of acetone and on the hydrazobenzene conversion in alcohol and other solvents in just the same way as in the case of esterification (Goldschmidt) and the decomposition of ethyl diazoacetate (Bredig). Water, to the extent of 0·5 per cent in acetone itself, depresses the velocity with which it absorbs bromine under the influence of acids to considerably less than one-half of its original value.

Proceeding from the most generally accepted view that free hydrogen ions are responsible for catalysis by acids, a strict mathematical expression applying to the state of an acid in a medium is easily developed. By means of this it is not difficult to show that all the generalisation of Ostwald and Arrhenius applying to the variations of conductivity and catalytic activity with volume and the measured degree of dissociation will be as true when the medium consists of, or contains, a mixture of bases as when it is neutral ; further, that all acids at infinite dilution in a given medium will exhibit the same equivalent catalytic activity. But this is mathematically true when the hydrogen ions in all cases are then made =0.

In order to connect these conclusions with the basic properties of common oxygenated solvents, a simple indicator method has been devised. The phenomena observed with water on the indicator salt in alcohol, simulate closely the effects of water on acid catalysis. Using this process in several media, Mr. R. W. L. Clarke reports, as a first approximation to the real relative affinities of some weak bases ; carbamide, 17 ; water, 1 ; ether, 0·12 ; ethyl alcohol, 0·06. The values are fairly concordant amongst themselves, and are of the expected order.

SOCIETY OF CHEMICAL INDUSTRY.

(London Section).

Ordinary Meeting, December 7th, 1908.

Dr. Lewkowitsch in the Chair.

"*Cellulose and Chemical Industry.*" By Messrs. Cross and Bevan.

This paper is a retrospect and a general forecast. Such a review is suggested by the synchronism of the date of the formation of the Society with the commencement of the wood-pulp (cellulose), and "artificial silk" or lustra-cellulose industries. In the generation which has elapsed, this latter industry has reached large dimensions ; the current production is estimated at 5000 tons per annum. The authors examine the basis of competition of these artificial or "chemical" fibres, with silk one the one hand, and vegetable (fibrous) "mechanical" textiles on the other. With further refinements of the processes, and further constitutional modifications of the colloidal cellulose, which are already shown to be attainable, new avenues of expansion of the industry are assured. Problems of fundamental importance to the flax, jute, and wood-pulp industries are briefly discussed. Generally, there is considerable activity in the more special developments of the cellulose industries, and a very large number of definite problems are presented to the chemist for investigation and solution. Manufacturers cannot be expected to take long forecasts, or to devote means to research beyond what is necessary for attacking proximate problems connected with routine. Chemists must adapt themselves to the situation, and find their own ways and means for work in one of the most fruitful and attractive fields of investigation.

"*The Viscosity of Indiarubber and Indiarubber Solutions, with particular reference to its bearing on the Strength or 'Nerve' of Crude Rubber.*" By P. Schidrowitz and H. A. Goldsbrough.

The authors have studied the viscosity of different crude rubbers in benzene solutions, and have correlated the viscosity curves and values with the figures obtained by tension (breaking, strain, &c.) experiments. The viscosity curves show that, beyond a certain concentration (which the authors call the "critical-point"), the curve becomes a straight line, but that the straight lines so obtained from different rubbers are not directly comparable. It is necessary, therefore, for purpose of comparison, to calculate a value from two points by the ordinary equation $y = mx + c$. The results obtained appear to show a distinct connection between viscosity and "nerve," weak rubbers yielding a flat, strong rubbers a steep curve. Assuming that some of the peculiar physical attributes of rubber are due to de- or re-polymerisation, the viscosity method seems likely to afford a useful means of measuring the molecular condition, and in any case of distinguishing between that which the authors term "mechanical" strength and "physical or chemical" nerve.

"*The Structure of Crude Indiarubber.*" (Preliminary Note). By P. Schidrowitz, Ph.D.

The author states that his experiments appear to warrant the important conclusions that the globules are not destroyed by coagulation of the latex, and that they continue to exist in the dry rubber, and are not removed even by dissolving the latter in benzene. Microscopic examinations of benzene solutions by means of the dark ground illumination method discloses the presence of bodies which, in size and general appearance, are strikingly similar to the

original globules of the latex, and the same applies to the spherical bodies observed in dry rubber obtained by different methods, including the evaporation of solutions. The presence of the globules, the author points out, may explain some of the more important physical properties of crude and, perhaps, of vulcanised indiarubber.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. cxlvii., No. 20, November 16, 1908.

Agricultural Use of Calcium Cyanamide.—A. Müntz and P. Nottin.—In experiments in which the quantities of cyanamide employed were ten to twenty times those which would be used in agricultural practice, the nitrifying oganisms appeared to be paralysed at first, and even a slight denitrification was observed. After a short time, however, the organisms became acclimatised, and nitrification proceeded normally. The decrease of activity is due to the cyanamide itself and not to the quicklime which it always contains. The results obtained in the nitrification experiments show that calcium cyanamide is one of the most active nitrogenous manures, being practically equivalent to ammonium sulphate. It can be applied either at the time of sowing or as a top dressing, but in the latter case it must be used only in rainy weather.

Volumetric Composition of Ammonia and Atomic Weight of Nitrogen.—Ph. A. Guye and A. Pintza.—The authors have determined the density of the gas N_2+3H_2, obtained from the decomposition of a given weight of NH_3, and have thence calculated the atomic weight of nitrogen. Taking O = 16 the atomic weight lies between 14·00 and 14·02, which confirms the value 14·01 adopted by the International Commission.

Fused Amorphous Alumina and the Production of Artificial Sapphires.—Louis Paris.—When oxides capable of giving a blue coloration are added to alumina fused before the blowpipe flame no coloration is produced. The oxides float on the surface of the alumina, without mixing with it or colouring it. If, however, the alumina used is not chemically pure but contains some hundredths of a foreign oxide, *e.g.*, lime, cobalt gives a blue coloration, and the optical properties of the alumina show that the latter is not crystalline but amorphous. The specimens of coloured alumina thus produced so closely resemble sapphires that even experts have been unable to distinguish them from the naturally occurring gems. With nickel yellow specimens have been obtained which rival the Ceylon sapphire.

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Berichte der Deutschen Chemischen Gesellschaft. Vol. xli, No. 15, 1908.

Hydrofluorides of Weak Organic Bases.—R. F. Weinland and F. Reischle.—A saturated alcoholic solution of hydrofluoric acid reacts with acetanilide and *p*-ethoxyacetanilide, giving hydrofluorides of the composition Acetanilide + 1HF and *p*-Ethoxyacetanilide + $3HF+2H_2O$. Similarly triphenylamine dissolves in saturated alcoholic strongly fuming hydrofluoric acid, and from the solution the monohydrofluoride slowly separates in the form of a pale green powder. It is not very stable, losing hydrofluoric acid in dry air. Diphenylamine gives di- and trihydrofluorides and aniline mono-, di, and tri-hydrofluorides. Azobenzene gives a compound which is fairly stable in a desiccator, and dimethylpyrone forms hydrofluorides, which are quite stable in dry air.

Molecular Condition of Fused Salts.—Richard Lorenz and F. Kaufler.—The similarity between the electrochemical behaviour of fused salts and solutions of salts suggests that they are in both cases in the same molecular condition, and the question arises how far fused salts conform to the laws of Arrhenius' theory for aqueous solutions. To decide this it is necessary to determine the molecular weights of the salts in the fused state. If it is true that the salt simply dissociates into its ions, the molecular weights observed must be lower than those which correspond to the chemical formulæ, as is the case with dilute aqueous solutions. If the molecular weight is greater complex ions must be formed and association must occur. The surface tension method was used to determine the molecular weights, and the results showed that salts in the fused state are complex compounds, the ions being complex ions, a result which seems to gain in probability when it is remembered that double salts such as those of lead chloride and alkali chloride, in which a complex anion of lead and chlorine is present, exist in a molten state.

Silicon Iodoform.—Otto Ruff.—Silicon iodoform may be obtained from silicon chloroform by converting the latter either into the nitrogen hydride SiNH by the action of liquid ammonia, or with aniline into the hydrotrianilide $SiH(NH.C_6H_5)_3$, and then treating these compounds with dry hydriodic acid in carbon disulphide or benzene solution. The second method gives the better yield, and is also more convenient. The nitrogen compound is similarly split up by hydrochloric and hydrobromic acids. Silicon iodoform is a colourless liquid which very readily forms silicon formic acid with water. It yields an oxyiodide with oxygen. It burns readily in air, and at a high temperature its vapour forms an explosive mixture with air.

Ferromagnetic Nitrogen Compounds of Manganese.—E. Wedekind and Th. Veit.—On heating manganese in a current of ammonia to the temperature of the oxyhydrogen blowpipe flame a relatively strongly magnetic preparation is obtained. The analysis of it gives results which correspond to the formula Mn_7N_2. It may be shown that whether this is actually a new compound or not the magnetisability of compounds of manganese and nitrogen increases as the amount of manganese increases. When powdered manganese is heated in dry hydrogen gas over a coal-gas blowpipe flame a molten mass is obtained which is feebly magnetic. The oxide obtained by heating manganese powder in a current of oxygen is not magnetic.

Spectrum of Neo-Erbium Oxide.—K. A. Hofmann and Günther Bugge.—The power of erbium oxide of forming a reflexion spectrum with sharp lines which are regularly grouped about definite maxima is not shared by the solid salts in general. The oxalate and the fluoride obtained by evaporation show bands similar to those of the dissolved nitrate or sulphate, although differences in intensity and position can be detected. With the dry sulphate lines appear as well as the bands, so that a transition from the band spectra of the salts to the line spectra of the oxide seems possible. Apparently the light-absorbing and emitting electrons of the erbium atom in the oxide perform far more regular oscillations than in compounds with acid residues or water molecules, and in the solid state the conditions of the freedom of the movement of the electrons are similar to those in dilute gases.

Constitution of Copper Acetylide.—Johannes Scheiber.—Copper acetylide exists in two forms, one anhydrous with the formula C_2Cu_2, and the other monohydrated $C_2Cu_2.H_2O$. The behaviour of the hydrated acetylide seems to harmonise best with the formula CH:C.Cu.Cu.OH, and Makowka's formula appears to be incorrect. Copper acetylide can be prepared in the pure state. The carbonaceous residue left when a preparation is dissolved in acids is not an impurity, but it is a humus-like substance the formation of which must be ascribed to secondary processes.

MEETINGS FOR THE WEEK.

TUESDAY, 29th. } Royal Institution, 3. (Christmas Lectures,
THURSDAY, 31st. } adapted to a Juvenile Auditory). "The Wheel
SATURDAY, Jan. 2nd. } of Life," by Prof. W. Stirling, M.D.,&c.

INDEX.

ABERDEEN University, 143
Aberystwyth, University College of Wales, 136
Acetophenone, fixation by benzoylacrylic acid, 210
Acetylacetone, products of condensation of chlorides of *o*- and *p*-nitrated benzile with, 60
Acid, aminophenylarsenic, isomeric, 7
arsenious, action of magnesium organic compounds on, 222
benzilic, preparation, 12
benzoylacrylic, fixation of acetophenone by, 210
chloroauric, action of silver nitrate on, 23
chromic, decomposition by hydrogen peroxide, 233
citric, 95
dicamphorylarsinic, 315
dioxy-3 . 4-butyric, lactone of, 47
glycuronic, simple test for, 24
hippuric, test for, 181
hydrazoic, preparation, 222
hydrochloric, affinity of alkaloids for, 277
hypophosphoric, molecular weight and hydrate of, 222
mellitic, rhodamines of, 253
1-methylcyclohexan-2-*ol*-carboxylic, cis- and trans-modifications of, and their conversion into 1-methyl-Δ^1-cyclohexene-4-carboxylic acid 230
1-methylcyclohexylidene-[4]-acetic, experiments on synthesis of, 268
nitric, 96
compounds of mercury cyanide with, 12
phosphoric, electrical conductivity of, 279
phosphorous, oxidation by iodine, 231
picric, heat of neutralisation by different aromatic bases in benzene, 83
succinic, determination in presence of fixed acids in wines and fermented liquids, 245
sulphuric, electrolytic properties of dilute solutions of, 98, 118, 127, 158
viscosity of fuming, 315
tannic, estimation, 316
a-triazopropionic, resolution of, 267
tungstic, and silica, separation, 294
Acid, vanadic, reduction by zinc and magnesium, 2
Acids in wines, determining the fixed and volatile, 162
optically active salts of containing adjacent unsaturated groups, 229
acetic and benzoic, heat of neutralisation by aniline in a benzene medium, 47
acetylenic, formation of 4-pyrone compounds from, 34
arsenic, action of alkalis on mono and dimethyl, and their iodine substitution products, 47
arsonic, aromatic, 268
campholic and isocampholic, direct transformation of borneol into, 84
carboxylic, synthesis of aromatic from hydrocarbons, 222
dithiodiglycollic and dithiodilactylic, esters of, 242
mellitic and pyromellitic, constitution of phthaleins of, 254
organic, electrolytic chlorination of salts of, 33
preparing mixed anhydrides of, 162
a-oximino-fatty, conductivities of, 231
phosphoric, molecular weights of determined by cryoscopy, 60
pinonic and pinic, active, 245
styphnic and picric, molecular compounds of, 280
sulphinic, 280
tannic and gallic, action of reducing agents on, 316
unsaturated, of benzene series, 254
Acridines, synthesis of complex, 243
Actinium and thorium emanations, diffusion of, 304
Affinity constants of bases as determined by aid of methyl-orange, 278
Agriculture, chemical industry in relation to, 257
"Air and Ventilation of Subways" (review), 280
Alcohols, action of metallic oxides on primary, 59, 83, 96
decomposition under catalytic action of live coals, 59
"Alkali Soils, their Nature and Reclamation" (review), 11
"Alkali, &c., Works, Annual Report on" (review), 221
Alkali metals, solutions of in liquid ammonia, 24
trithionates and tetrathionates of, 243
nitrates, crystallisation of solutions of, 242
Alkalis, action on ethyl sodium thiosulphate, 12
on mono and dimethyl arsenic acids and their iodine substitution products, 47
on sodium alkyl thiosulphates 34
compounds of mercury cyanide with, 12
caustic, action on derivatives of parani rotoluene, 243
Alkaline chloroiridates and chloroiridites, 31
chloroiridites, preparation, 60
solutions of zinc salts, action of hydrogen sulphide on, 40
Alkaloids, affinity for hydrochloric acid, 277
Alkyl halides and magnesium, interaction, 232
nitrates, reduction to nitrites, 48
Allantini, L., citric acid, 95
Allen, H. S., graphic method of dealing with refracting surfaces, 303
Allender, A., ozokerite, paraffin and cerasin waxes, 210
Alloy, potassium-sodium, photoelectric properties of, 268
"Alloys, Analysis of Ashes and" (review), 196
Alloys of silicon and silver, 305
quantitative estimation of lead in, 1
electro-metallurgical, new applications of, 15
Aloesol, 294
Altmayer. V., and M. Mayer. (*See* Mayer, M.)
Alumina, amorphous, fused, 318
Aluminium and iron groups, analysis, 6, 16, 32, 41, 55, 71, 81, 92, 107, 160, 171, 181, 194, 208, 219, 228, 239, 251, 264, 273, 291, 300, 311
rapid method of, 211
Anhydride, tungstic, and silica, separating, 47
Anhydrides of organic acids, preparing mixed, 162
Anselmino, O., picrates, 233
Antimony and arsenic associated with copper, iodometric determination, 51
and tin, separation, 230
Apocynin, synthesis of, 21
Apparatus, laboratory, 49
Appleby, M. P., "Fundamental Conceptions of Chemistry" (review), 11
Argon, preparation from air, 40
Amido groups, action of chlormethyl sulphate on, 11
Aminoalkyl esters, relation between chemical constitution and physiological action in, 254
Ammonia, action on phosphorus, 11
and amines, separation by means of boiling absolute alcohol, 23
and carbon monoxide, dissociation temperature, 197
production from atmospheric nitrogen by means of peat 163
solubility of silver iodide in, 46
sulphate, 172
volumetric composition, 318
Ammonium compounds, double dissociation of quaternary, 48
persulphate and sodium peroxide, reaction between, 197
Amygdalin, hydrolysis by emulsin, 35
Amyl ether and magnesium methyl iodide, crystalline compound of, 44
a-Amyrine, identity of ilicic alcohol with, 305
"Analysis of Ashes and Alloys" (review), 196
"Analysis, Chemical" (review), 196
"Analysis, Chemico-technical, Post's" (review), 23
"Analysis, Qualitative, and Practical Chemistry, Treatise on" (review), 45
"Analysis, Quantitative, by Electrolysis" (review), 197
Analysis, qualitative, system of for common elements, 6, 16, 32, 41, 55, 71, 81, 92, 107, 160, 171, 181, 194, 208, 219, 228, 239, 251, 264, 273, 291, 300, 311
rapid method of, 211
Anhydride, tungstic, and silica, separating, 47
Anhydrides of organic acids, preparing mixed, 162
Anselmino, O., picrates, 233
Antimony and arsenic associated with copper, iodometric determination, 51
and tin, separation, 230
Apocynin, synthesis of, 21
Apparatus, laboratory, 49
Appleby, M. P., "Fundamental Conceptions of Chemistry" (review), 11
Argon, preparation from air, 40

Arkansas, electroscopic determination of the radium present in some "tufa" deposits from Hot Springs, 199
Armstrong, H. E., studies of the processes operative in solutions, 1
Armstrong College, 140
Arnold, H. R., and J. Houben. (*See* Houben, J.)
Arnvaut, G., alloys of silicon and silver, 305
Arsenic, action on cobalt, 179
and antimony associated with copper, iodometric determination, 51
mercurous nitrate as microchemical reagent for, 280
micro-chemical reactions of, 245
organic derivatives of, 315
chloride, action on cobalt, 179
ammoniacal, 46
telluride, 60
trichloride, action on nickel and on arseno-nickels, 166
Arsenite, action on thiosulphonic acid salts, 281
Arseno-nickels, action of arsenic trichloride on, 166
Arsine, action of selenium and tellurium on, 13
Arthur, W., and E. de M. Campbell. (*See* Campbell, E. de M.)
Arzalier, L., researches on acid sulphates of potassium, 96
"Ashes and Alloys, Analysis of" (review), 196
Assay of telluride ores, 180
"Assaying, Text-book of" (review), 22
Atacamite in copper ores, 132
Atomic volumes of phosphorus, 256
weight of chlorine, 97
lead, 64, 78
nitrogen, 305
pantogen, 294
silver, 305
weights, absence of exact relations among, 178
method of calculating, 215
of hydrogen and chlorine, 256
report of committee on, 192 204
Auger, V., action of alkalis on mono and dimethyl arsenic acids and their iodine substitution products, 47
Auld, S. J. M., hydrolysis of amygdalin by emulsin, 35
Austin, P. C., synthesis of complex acricines, 243
Azomethine compounds, colour and constitution, 267
Azoxybenzenes, products of reduction of, 255

BADDILEY, J., and A. G. Green. (*See* Green, A. G.)
Baker, F., blue ink, 234
Baly, E. C. C., J. N. Collie, and H. E. Watson, relation between absorption spectra and chemical constitution, 315
and C. H. Desch, relation between absorption spectra and chemical constitution, 22
and Effie G. Marsden, relation between absorption spectra and chemical constitution, 278
and K. Schaefer, relation between absorption spectra and chemical constitution, 254
and W. B. Tuck, relation between absorption spectra and chemical constitution, 266
Bangor, University College of North Wales, 136
Barbier, P., and V. Grignard, active pinonic and pinic acids, 245
Barger, G., action of phosphorus pentachloride on the methylene ethers of catechol derivatives, 278
Barger, G., and A. J. Ewins, synthesis of thionaphthen derivatives from styrenes and thionyl chloride, 278
Barium and strontium oxides, hydrates of, 120
nitrites, molecular volumes of, 279
sulphate, colloidal, 46, 310
Barlow, W., and W. J. Pope, polymorphism, 231
Barometer, sensitive temperature-compensated, 50
Barrowcliff, M., F. L. Pyman, and F. G. P., Remfry, aromatic arsonic acids, 268
Bars, lateral vibration and deflection of clamped-directed, 9
Bases, characterisation of primary, secondary, and tertiary with 1:5-dibrompentane, 48
Batez, A., consumption of sodium nitrate, 83
Battersea Polytechnic, 147
Baubigny, H., solubility of silver iodide in ammonia, 46
Bauer, E., and A. Haller. (*See* Haller, A.)
Baxter, G. P., and J. H. Wilson, revision of the atomic weight of lead, 64, 78
Beans, H. T., and F. J. Metzger. (*See* Metzger, F. J.)
Belfast, Queen's College, 144
Bellini, E., and A. Tosi, experiments on a directive system of wireless telegraphy, 8
Belloc, G., gases occluded in a special nickel steel, 162
Benzaldehyde, velocity of reaction of bromine on, 198
Benzamide, condensation of, 268
Benzene series, oxidations of hydrocarbons of, 241
unsaturated acids of, 254
Benzeneazo-2-pyridone, 33
Benzile, *o*- and *p*-nitrated, condensation of chlorides of with acetylacetone, 60
Benzoin type, formation of ethers from compounds of, 231
Beringer, C. and J. J., "Text-book of Assaying" (review), 22
Berry, L. H., products of reduction of azoxybenzenes, 255
Bertheim, A., isomeric aminophenylarsenic acid, 7
Bertheaume, J., separation of ammonia and amines by means of boiling absolute alcohol, 23
Bertrand, G., new crystallised sugar, perseulose, with seven carbon atoms, 117
and G. Weisweiller, constitution of vicianine, 162
Beryllium. (*See* Glucinum)
Besson and Rosset, MM., ammoniacal arsenic chloride, 46
Biltz, H., crystallised boron, 198
W., cerium sulphides, 280
Birkbeck College, 148, 162
Birmingham University, 138
Bismuth, electrolytic determination, 202
telluride, 60
Blackburn Municipa Technical School, 148
Blaise, E. E., and I. Herman, *β*-alcohol *a* - *a* - dialcoholated ketones, 47
Blanchard, A. A., "Synthetic Inorganic Chemistry" (review), 58
Block, E. and L., ionisation by phosphorus and phosphorescence, 305
L., constitution of hydrodisulsulphide and hydrotrisulphide, 24
and F. Hohn, hydrogen persulphide, 24
hydrodisulphide, 24
hydrotriaulphide, 24
Blount, B., Fellowship of the Chemical Society, 130
Bloxam, A. G., compulsory working of patents, 161
Bloxam, W. P., "Research Work on Indigo" (review), 45
Boae, W. A., and H. F. Coward, direct union of carbon and hydrogen, 265
thermal decomposition of hydrocarbons, 20
"Books, New Scientific and Industrial" (review), 58
Borax, platinum in so-called pure, 210
Borneol, direct transformation into campholic and isocampholic acids, 84
Boron, crystallised, 198
nitride, preparation, 48
thiocyanate, 315
Borough Polytechnic Institute, 147
Borrowman, G., some observations on the assay of telluride ores, 180
Bougault, J., fixation of acetophenone by benzoylacrylic acid, 210
Messinger and Vortmann's method of estimating phenols, 60
new method of preparing mixed anhydrides of organic acids, 162
Bradford, City of, Technical College, 138
Bray, W. C., A. A. Noyes, and E. B. Spear. (*See* Noyes, A. A.)
Brill, O., and C. de B. Evans, use of micro-balance for the determination of electrochemical equivalents and for the measurement of densities of solids, 229
Bristol, Merchant Venturers' Technical College, 138
University College, 137
British Association, Inaugural Address of the President, 109
Chemical Section Address, 121
Officers, &c., 131
Bromination experiments with diazobenzene perbromides, 198
Bromine, action on ether, 280
on *β*-hydrindone, 231
velocity of reaction of on benzaldehyde, 198
wandering of in transformation of nitroaminobromobenzenes, 165
Bronzes, high tension, 273
Browne, F., estimation of graphite, 51
Browning, P. E., and H. E. Palmer, estimation of cerium in presence of other rare earths by action of potassium ferricyanide, 106
Brucine oxidation, 12
Bryant, E. G., platinum in so-called pure borax, 210
women and the Chemical Society, 173
Bugge, G., and K. A. Hofmann (*See* Hofmann, K. A.)
Bulow, C., and H. Schmachtenberg, bromination experiments with diazobenzene perbromides, 198
Bunsen, Robert, monument to, 293
Burt, F. P., and R. W. Gray. (*See* Gray, R. W.)
Butler, G. M., "Pocket Handbook of Minerals" (review), 58
Buttle, B. H., and J. T. Hewitt, solubility of silver chloride in mercuric nitrate solution, 22

CÆSIUM dicalcium sulphate, 17
Calcium boride, preparation, 48
cyanamide, agricultural use of, 318
hydride, methane syntheses with, 234
hydroxide and milk sugar, products from, 210
Calcium nitrites, molecular volumes of, 279
sulphates, neutral triple, 5
Calhane, D. F., comparative oxidising power of sodium peroxide and its use in qualitative analysis, 206
Cambridge University, 133
honours for men of science, 7
Campbell, E. de M., and W. Arthur, determination of nickel and chromium in steel, 38
Camphor, condensation with mercuric iodide, 314
"Camphor, Italian" (review), 186
Canadian hemp, constituents of, 21
Carbides, formation, 279
Carbon and hydrogen, direct union, 265
hydrogen, and oxygen, thermochemical relations of, 46, 82
molecule, constitution, 37, 72
dioxide, decomposition by silent electric discharge, 316
influence of colloids and colloid suspensions on solubility of in water, 163
monoxide and ammonia, dissociation temperature of, 197
and cobalt, volatile compound of, 165
sub-oxide, 281
Cardiff, University College of South Wales and Monmouthshire, 137
Carre, P., lactone of dioxy-3.4-butyric acid, 47
Cart, John Trevor (obituary), 196
Cassie, W., accurate method of measuring moments of inertia, 304
"Catalogue of Lewis's Medical and Scientific Circulating Library" (review), 83
Catalytic reductions with colloidal palladium and platinum, 186
Caulophyllum thalictroides, fruit of, 190
Cell, primary voltaic of the Daniell type, 102
Cellulose, action of cold caustic soda solution on, 234
and chemical industry, 317
Cerium, estimation in presence of other rare earths, 106
sulphides, 280
Chapman, D. L., and H. E. Clarke. (*See* Clarke, H. E.)
Chattaway, F. D., action of chlorine upon urea, 285
of halogens on aromatic hydrazines, 187
alternative structure for the supposed stereoisomeric *a*-osazones, 33
constitution of the diazonium perbromides, 21
some reactions of dichloro urea, 166
Chelsea, South-Western Polytechnic, 148
"Chemical Analysis" (review), 196
"Chemical-technical Analysis, Posts" (review), 23, 232
"Chemical Novelties for 1908" (review), 23
Chemical constitution and absorption spectra, relation between, 22, 254, 266, 278, 315
and physiological action, relation between in substituted aminoalkyl esters, 254
and viscosity, relation between 256, 266
industry in relation to agriculture, 257
publications in America in relation to chemical industry, 75
Society, 17, 33, 35, 58, 94, 130, 173, 229, 241, 245, 252, 265, 277, 314
Research Fund, 258
Chemicals used for assaying, platinum metals in, 104
"Chemist, the Works" (review), 196

"Chemistry and Biology of the Secretions of Plants" (review), 120
"Chemistry, Fundamental Conceptions of" (review). 11
"Chemistry, Analytical, Scientific Foundations of" (review), 45
"Chemistry, Colloid, and Photography" (review), 45
"Chemistry, Inorganic, General" (review), 186
"Chemistry, Inorganic, Synthetic" (review), 58
"Chemistry, Pharmaceutical, Report of Recent Advances in, and Therapeutics" (review), 270
"Chemistry, Physical, Laboratory Exercises in" (review), 22
"Chemistry, Technical, Steam in" (review), 196
Chemistry, Applied, International Congress of, 24
colloidal, 152, 167, 175
forensic, lectures on, 241
"Chemists and Druggists, Kelly's Directory of" (review), 45
Chlorides, anhydrous, action on tellurium and tellurium dioxide, 4
chromous, isomeric, 256
Chlorination, electrolytic, of salts of organic acids, 33
of para-nitroaniline, 255
Chlorine, action on urea, 285
atomic weight, 97, 256
derivatives of pyridine, 266, 267
Chlormethylsulphate, action on amino groups, 11
4-Chloroacenaphthene, 279
Cholestenone, 22
Cholesterol, action of fused potassium hydroxide and of hydrogen peroxide on, 242
group, chemistry of, 242, 267
Chrome alum, 305
Chromium, determination in steel, 38
estimation as silver chromate, 101
formic and acetic acid salts of, 282
oxides, magnetic, 78
tetroxide compounds, 282
Cirencester, Royal Agricultural College, 139
Clarke, F. W., annual report of committee on atomic weights, 192, 204
H. E., and D. L. Chapman, measurement of a homogeneous chemical change in a gas, 230
Classen, A., "Quantitative Analyse durch Elektrolyse" (review), 197
Clayton, A., coumarin condensation, 268
Clowes, F., "Treatise on Qualitative Analysis and Practical Chemistry" (review), 45
Coals of South Wales, geological survey on, 12
Cobalt, action of arsenic chloride and of arsenic on, 179
and carbon monoxide, volatile compound of, 165
and nickel, detection when present together, 24
Cobaltinitrites, studies on, 255
Cocksedge, H. E., boron thiocyanate, 315
tellurium dicyanide, 315
Collie, J. N., E. C. C. Baly, and H. E. Watson. (*See* Baly, E. C. C.)
"Colloids, Contributions to the General Chemistry of" (review), 46
"Colloids, Introduction to the Chemistry of" (review), 293
Colloids and colloid suspensions, influence on solubility of carbon dioxide in water, 163
Colour and fluorescence, relationship to constitution, 253
Colouring matters in solution, 258
of stilbene group, 243
Compounds, cyclic, ultra-violet fluorescence in, 233
optically active, influence of solvents on rotation of, 257
organic, catalytic dehydration of, 23
Comstock, D. F., indestructibility of matter and the absence of exact relations among the atomic weights, 178
Condensation of camphor with mercuric iodide, 314
of chlorides of *o* and *p*-nitrated benzile with acetylacetone, 60
of sodium benzylate with propyl, butyl, and isoamyl alcohols, 60
Conductivity, electrical, of phosphoric acid, 279
Conductor of uniform thickness whose breadth suddenly changes, resistance of, 10
Constants, affinity of bases, as determined by aid of methyl-orange, 278
thermal, of aromatic substances, calculation, 80
Constitution, relationship of colour and fluorescence to, 253
Copaux, H., and E. Defacqz. (*See* Defacqz, E.)
Copper, action of radium on, 256
iodometric determination of arsenic and antimony associated with, 51
ores, atacamite in, 132
acetylide, constitution, 318
salts, action of radium emanation on solutions of, 157
Coprosterol, 242
Cork, Queen's College, 145
Cornus sericea, fruit of, 190
Cotton thread, rotting, 174
Coumarin condensation, 268
Cousin, H., and H. Hérissey, oxidation of isoeugenol, 161
Cowap, M. D., L. Mond, and H. Hirtz. (*See* Mond, L.)
Coward, H. F., and W. A. Bone. (*See* Bone, W. A.)
Cowles, H. W., jun., preparation of a solution for making standard solutions of sodium hydroxide, 108
Creeth, N. A., and J. F. Thorpe, action of bromine on *β*-hydrindone, 231
Crewdson, Mary S., and J. F. Spencer. (*See* Spencer, J. F.)
Crompton, H., and Eva R. Cyriax, 4-chloroacenaphthene, 279
Crookes, Sir W., 7
scandium, 274, 283, 295, 307
Cross and Bevan, Messrs., cellulose and chemical industry, 317
"Crystal Drawing, Hints for" (review), 293
Crystallisation explosive, 27, 59
of solutions of alkali nitrates, 242
Crystals, liquid, 47
Cunningham, Mary, and F. M. Perkin, studies on the cobaltinitrites, 255
Curie, Mdme., formation of mists in presence of radium emanation, 156
and Mdlle. Gleditsch, action of radium on solutions of copper salts, 157
Curtius, T., and E. Rimele, action of hydrazine hydrate on bisdiazoacetic ester, 234
Cyanide, action on thiosulphonic acid salts, 281
Cyanides, metallic, reactions of phenylhydrazine with, 34
Cyriax, Eva R., and H. Crompton, (*See* Crompton, H.)

DARWIN, F., British Association, Presidential address, 109
Daudel, M., and M. Tiffeneau. (*See* Tiffeneau, M.)
Dawson, H. M., formation of polyiodides in nitrobenzene solution, 35
Dawson, H. M., and C. G. Jackson, formation of polyiodides in nitrobenzene solution, 256
D'Ans, J., cæsium dicalcium sulphate, 17
neutral triple sulphates of calcium, 5
De Forcrand, M., hydrates of strontium and barium oxides, 120
Dean, W. M., characteristic test for hippuric acid, 181
Deason, E. J., nitric acid, 96
Debierne, A., present state of our knowledge of radio-activity, 235, 247, 259, 271, 289, 300
Decomposition of certain minerals and industrial products by means of sodium peroxide and metallic sulphides, 61, 76
of chromic acid by hydrogen peroxide, 233
Defacqz, E., new method of separating silica and tungstic anhydride, 47
and H. Copaux, new iodide of titanium 83
Dehn, W. M., and S. F. Scott, some characteristic colour reactions produced by sodium hypobromite, 200
Dehydration, catalytic, of organic compounds, 23
Dehydroisoeugenol, 161
Delépine, M., alkaline chloroiridates and chloroiridites, 31
Deniges, G., mercurous nitrate as a micro-chemical reagent for arsenic, 280
micro-chemical reactions of arsenic applicable in forensic chemistry, 245
Densities of solids, use of micro-chemical balance for measurement of, 229
Density, determination by means of ordinary pea-shaped specific gravity bot
of gases, 53, 68
Desch, C. H., and E. C. C. Baly. (*See* Baly, E. C. C.)
Dewar, Sir J., rate of production of helium from radium, 188
Diazobenzene perbromides, bromination experiments with, 198
Diazo-compounds, researches on, 60
Diazonium perbromides, constitution, 21
1.5-Dibrompentane, characterisation of primary, secondary, and tertiary bases with, 48
3.5-Dichloropyridine, preparation and orientation, 266
Dichloro urea, production, 285
reactions of, 166
Dick, H., and W. Herz. (*See* Herz, W.)
Dicyclopentadiene, action of nitrous gases on, 33
Diels, O., and L. Lalin, carbon suboxide, 281
Dierbach, R., "Der Betriebs-Chemiker" (review), 196
Diphenylmethane derivatives, constitution, 47
Dissociation, double, of quaternary ammonium compounds, 48
temperature of ammonia and carbon monoxide, 197
Disulphides, preparation, 34, 229, 242
α-Disulphones, aromatic, 231
Disulphoxides, preparation and constitution, 233
Divers, E., must women be denied Fellowship of the Chemical Society, 94
Dixon, A. E., and J. Taylor, study of the constitution and properties of the rhodanides of inorganic radicles, 279
Doree, C., and J. A. Gardner, cholestenone, 22
coprosterol, 242
Douglas, L. M., impressions of the First International Food Congress, 184
Dublin, Royal College of Science 146
University, 134
Duboux, M., and P. Dutoit. (*See* Dutoit, P.)
Dubreuil, L., method of calculating atomic weights, 245
true atomic weight of silver from Stas's experiments, 305
Ducelliez, F., action of arsenic chloride and of arsenic on cobalt, 179
Dundee, University College, 142
Dunstan, A. E., and F. B. Thole, relation between viscosity and chemical constitution, 256
and J. A. Stubbs, relation between viscosity and chemical constitution, 266
and R. W. Wilson, viscosity of fuming sulphuric acid, 315
Dutoit, P., and M. Duboux, analysis of wines, 96, 174
Duval, H., constitution of derivatives of diphenylmethane and preparation of ortho-diamino-compounds, 47
researches on diazo-compounds, 60
"Dyeing and Cleaning" (review), 257
Dyes soluble in petrol, 162
Dynamic isomerism, 155

EARTH, radio-active changes in, 73
Eckenstein, E., "Développement et Progrès de la Fabrication du Malt pendant les Quarante Dernières années" (review), 10
Edgar, E. C., atomic weight of chlorine, 97
G., estimation of iron and vanadium in the presence of one another, 80
and F. A. Gooch (*See* Gooch, F. A.)
Edinburgh, Heriot-Watt College 144
University, 144
Egg-yolk, proteins of, 231
Eisner, F., and O. Ruff. (*See* Ruff, O.)
Elborne, W., and C. M. Warren, note on the quantitative estimation of lead in alloys, 1
Eldredge, C. G., and Edith Stockton. (*See* Stockton, E.)
Elements, potential energy of, 11, 23, 46, 59, 120, 174
system of qualitative analysis for common, 6, 16, 32, 41, 55, 71, 81, 92, 107, 160, 171, 181, 194, 208, 219, 228, 239, 251, 264, 273, 291, 300, 311
Ellis, H. R., formation of graphite by the interaction of magnesium powder and carbonates, 309
Energy, potential, of the elements, 11, 23, 46, 59, 120, 174
Equivalents, electro-chemical, use of micro-balance for determination of, 229
Ergosterin and fungisterin, 79
Ester catalysis, 317
bisdiazoacetic, action of hydrazine hydrate on, 234
Esters of dithiodiglycollic and dithiodilactylic acids, 242
Ether, action of bromine on, 280
Ethers, formation from compounds of benzoin type, 231
benzoylacetic, preparation, 84
Ethyl acetoacetate, isomerism of, 127
pyruvate, action on paratoluidine, 96
sodium thiosulphate, action of alkalis on, 12
Ethylene derivatives, methylation in, 174
Evans, C. de B., and O. Brill. (*See* Brill, O.)

Everatt, R. W., and H. O. Jones, effect of constitution on the rotatory power of optically active nitrogen compounds, 255
Evieux, M., and L. Vignon. (*See* Vignon, L.)
Ewins, A. J., and G. Barger. (*See* Barger, G.)
Exhibition, Physical Society, 282
Explosive crystallisation, 27, 59
"Explosives, Report of His Majesty's Inspectors of" (review), 280

"FABRIC Printing and Allied Industries, Annual Report on the Progress of" (review), 197
Falcke, V., and R. Schenck. (*See* Schenck, R.)
Faraday Society, 22
Farrell, F. J., "Dyeing and Cleaning" (review), 257
Feimann, E., colloidal barium sulphate 310
Fermentation, alcoholic, factors which influence rate of, 175
Ferro-alloys, opening up, 258
production of, 230
Fierz, H. E., and M. O. Forster, (*See* Forster, M. O.)
Findlay, A., influence of colloids and colloidal suspensions on the solubility of carbon dioxide in water, 163
Finnemore, H., constituents of Canadian hemp, 21
new synthesis of apocynin, 21
Fischer, A., "Die Chemische Analyse" (review), 196
F., and O. Ringe, preparation of argon from the air by means of calcium carbide, 40
Fisher, K., and W. H. Perkin, jun., experiments on the synthesis of the terpenes, 267
Fitzgerald, E., and A. Lapworth, ester catalysis and a modification of the theory of acids, 317
Fleming, R., photo-electric properties of potassium-sodium alloy, 268
and F. G. Pope. (*See* Pope, F. G.)
Fleming-Struthers, R. de J., reactions of phenylhydrazine with metallic cyanides and other salts, 34
and J. E. Marsh, action of mercuric iodide on ketones in alkaline solution, 314
condensation of camphor with mercuric iodide, 314
double salts of potassium iodide with mercuric iodide and dimercuriodocamphor in organic solvents, 314
Fluorene, sodium compound of, 233
Fluorescence and colour, relationship to constitution, 253
of platinocyanides, 34
ultra-violet, in cyclic compounds, 233
Fluorscheim, B., chlorination of para-nitroaniline, 255
Food Congress, impressions of the First International, 184
Formaldehyde, formation in solutions of cane sugar, 288
Formalin in milk, determination, 247
Forster M. O., and H. E. Fierz, triazo-group, 267
Fosse, R., constitution of tetramethyldiaminobenzhydryl methylene compounds, 47
Fra çois, M., double phosphate of magnesium and monomethylamine, 47
modification of method of preparing monomethylamine, 258
notes on two methods of preparing monomethylamine, 170
Frank, A., chemical industry in relation to agriculture, 257
Promm, E., lowest oxides of sulphuretted hydrogen, 281
Fruit of the Caulophyllum thalictroides, and Cornus serica, 190
Fungisterin and ergosterin, 79
Furnace, electric induction, Rochling-Rodenhauser, 29

GALWAY, Queen's College, 146
Gardner, J. A., and C. Doree. (*See* Doree, C.)
W. M., and H. H. Hodgson, action of iodine on phenols and a modified process for the estimation of tannic acid, 316
action of reducing agents on tannic and gallic acids, 316
Gas burette, new form, 255
measurement of a homogeneous chemical change in a, 230
mixtures, detection of ozone, nitrogen peroxide, and hydrogen peroxide in, 65
"Gases. Compressed and Liquefied" (review), 270
Gases, density of, 53, 68
occluded in a special nickel steel, 162
nitrous, action on dicyclopentadiene. 33
Gazdar, Maud, and S. Smiles, interaction of hydrogen dioxide and sulphides, 256
Gernez, D., triboluminescence of racemic compounds, 83
Gerum, J., and C. Paal. (*See* Paal, C.)
Getman, F. H., "Laboratory Exercises in Physical Chemistry" (review). 22
Gibson, C. S., some molecular compounds of styphnic and picric acids, 280
Giglioli, I., "La Canfora Italiana" (review), 186
Gilbert, G. K., "San Francisco Earthquake and Fire of April 18, 1906" (review), 45
Gilmour, C., and J. C. Irvine. (*See* Irvine, J. C.)
Giran, H., molecular weights of phosphoric acids determined by cryoscopy, 60
Glasgow and West of Scotland Technical College, 145
"Glass, &c., Decoration of" (review). 23
Glass, effects of sunlight upon colourless, 100
preparation of dark coloured, 281
Gleditsch, Molle., and Mdme. Curie. (*See* Curie, Mdme.)
Glucinum analysis, 6, 16, 32, 41, 55, 71, 81, 92, 107, 160, 171, 181, 194, 208, 219, 228, 239, 251, 264, 273, 291, 300, 311
Glucose derivatives, constitution of, 229
anilide, 229
hydrazone, 229
oxime, 229
Gold, action of radium on, 256
preparation of fulminating, 23
Goldsbrough, H. A., and P. Schidrowitz. (*See* Schidrowitz, P.)
Gooch, F. A., and G. Edgar, reduction of vanadic acid by zinc and magnesium, 2
and L. H. Weed, estimation of chromium as silver chromate, 101
Gortner, R. A., some effects of sunlight upon colourless glass, 100
Grapbite estimation, 51
formation by interaction of magnesium powder and carbonates, 309
Gray, R. W., and F. P. Burt, relative atomic weights of hydrogen and chlorine, 256
Green, A. G., constitution of the salts of phthaleins and the cause of colour in the triphenylmethane series, 253
and J. Baddiley, colouring matters of the stilbene group, 243
W. H., notes on laboratory apparatus, 49
studies on the viscosity and conductivities of some aqueous solutions, 230
Greenwood, H. C., production of ferro-alloys, 230
reduction of refractory oxides by carbon, 230
Grignard, V., and P. Barbier. (*See* Barbier, P.)
Grossman, H., and W. Heilborn, detection of nickel and cobalt when present together, 24
Guerbet, M., direct transformation of borneol into campholic and isocampholic acids, 84
three new primary methods resulting from the condensation of sodium benzylate with propyl, betyl, and isoamyl alcohols, 60
Gutmann, A., action of alkalis on ethyl sodium thiosulphate, 12
of arsenite and cyanide on thiosulphonic acid salts, 281
reduction of alkyl nitrates to nitrites by reducing salts in alkaline solution, 48
Guye, P. A., researches on the density of gases, 53, 68
and A. Pintza, volumetric composition of ammonia and atomic weight of nitrogen, 318

HAEFFNER, K., and C. Harries. (*See* Harries, C.)
Haller, A., and E. Bauer, products of the reaction of sodamide on ketones, 305
Halogen derivatives, organic, and metals of aluminium group, interaction, 241
Halogens, action on aromatic hydrazines, 187
Harden, Dr., lectures on milk, 205
J., recent developments of the Kjellin and Rochlin-Rodenhauser electric induction furnaces, 29
Harding, V. J., W. N. Haworth, and W. H. Perkin, jun., experiments on the synthesis of 1-methylcyclohexylidene-4-acetic acid, 268
Harries, C., and K. Haeffner, ozonides of simple olefines, 246
Hartley, W. N., lithium in radioactive minerals, 151
Haworth, W. N., V. J. Harding, and W. H. Perkin, jun. (*See* Harding, V. J.)
Hay, J. G., and R. Meldola. (*See* Meldola, R.)
Heath, F. H., iodometric determination of arsenic and antimony associated with copper, 51
Hehner's test for formaldehyde in saccharin mixtures, 288.
Heilborn, W., and H. Grossman. (*See* Grossman, H.)
Helium, liquefaction of, 37
rate of production from radium, 188
Heller, G., reduction of nitrocompounds with zinc dust and acetic acid, 222
Hemp, constituents of Canadian, 21
Henry, L., methylation in ethylene derivatives, 174
relative stability of the cyclic poly-carbon groups, 221
Hérissey, H., and H. Cousin. (*See* Cousin, H.)
Herman, I., and E. E. Blaise. (*See* Blaise, E. E.)
Herz, W., and H. Dick, velocity of reaction of bromine on benzaldehyde, 198
Hewitt, J. T., and B. H. Buttle. (*See* Buttle, B. H.)
Hilditch, T. P., aromatic *a*-disulphones, 231
relation between unsaturation and optical activity, 229, 241
and S. Smiles. (*See* Smiles, S.)
Hill, A. E., new form of gas burette, 255
of potash bulb, 38
Hillebrand, W. F., influence of fine grinding on the water and ferrous-iron content of minerals and rocks, 205, 215
Hinrichs, G. D., determination of the atomic weight of the simple ponderable substance, pantogen, 294
Hinsberg, O., preparation and constitution of sulphoxides and disulphoxides, 233
Hirtz, H., L. Mond, and M. D. Cowap. (*See* Mond, L.)
Hodgson, H. H., and W. M. Gardner. (*See* Gardner, W. M.)
Hofmann, K. A., and G. Bugge, spectrum of neo-erbium oxide, 318
and H. Wagner, compounds of mercury cyanide with alkalis and with nitric acid, 12
Hohn, F., and I. Bloch. (*See* Bloch, I.)
Holle, W., and A. Stock. (*See* Stock, A.)
Holmes, J. A., "San Francisco Earthquake and Fire of April 18, 1906" (review), 45
Holt, A., jun., decomposition of carbon dioxide by the silent electric discharge, 316
Houben, J., and H. R. Arnold, action of chloromethylsulphate on amino-groups, 11
"House Painting" (review), 258
Humphrey, R. L., "San Francisco Earthquake and Fire of April 18, 1906" (review), 45
Hydrates of strontium and barium oxides, 120
Hydrazine hydrate, action on bis-diazoacetic ester. 234
Hydrazines, aromatic, action of halogens upon, 187
β-Hydrindone, action of bromine on, 231
Hydrocarbons, aromatic, 266
of benzene series, oxidations of, 241
thermal decomposition of, 20
to prepare, 186
Hydrodisulphide, 24
constitution, 24
Hydrofluorides of weak organic bases, 318
Hydrogen and carbon, direct union of, 265
and oxygen, thermo-chemical relations of, 46, 82
and nickel, relations between, 234
atomic weight, 256
making pure, 173
passage through a palladium septum, 254
sulphuretted, lowest oxides of, 281
dioxide and sulphides, interaction, 256
ions, conception of in catalysis, salt formation and electrolytic conduction, 317
peroxide, action on cholesterol, 242
decomposition of chromic acid by, 233
in gas mixtures, detection, 65
persulphide, 24, 198
sulphide, action on alkaline solutions of zinc salts, 40
Hydrogenation of polyphenols, 23

Hydrolysis of amygdalin by emulsin, 35
of iron perchloride, 294
Hydrotrisulphide, 24
constitution, 24

ILICIC alcohol, identity with *a*-amyrine, 305
Imperial College of Chemistry and Pharmacy, 148
of Science and Technology, 135
Indiarubber and indiarubber solutions, viscosity of, 317
structure of crude, 317
"Indigo, Research Work on" (review), 45
Inductance of two parallel wires, 10
Industrial products, decomposition by means of sodium peroxide and metallic sulphides, 61, 76
Inertia, measuring moments of, 304
Inglis, J. K. H., and Lottie E. Knight, conductivities of the *a*-oximino-fatty acids, 231
and F. Wootton, electrolytic chlorination of the salts of some organic acids, 33
Institute of Chemistry, 146
examinations pass list, 48, 282
Iodide, mercuric, action on ketones in alkaline solution, 314
condensation of camphor with, 314
Iodine, action on phenols, 316
oxidation of phosphorous acid by, 231
Iodoaceto nitrile, synthesis of, 48
Iodohydrines of naphthalene series, migration of naphthyl group in, 258
Ionisation by phosphorus and phosphorescence, 305
"Ions, Theory of" (review), 94
Iron and aluminium groups, analysis, 6, 16, 32, 41, 55, 71, 81, 92, 107, 160, 171, 181, 194, 208, 219, 228, 239, 251, 264, 273, 291, 300, 311
and manganese, separation, 105
and Steel Institute, 108, 149
and vanadium, estimation in presence of one another, 80
relation between magnetic and chemical properties of complex salts containing, 83
rusting of, 20
ferrocyanide, oxydasic phenomena produced by colloidal, 280
perchloride, hydrolysis of, 294
Irvine, J. C., and R. Gilmour, constitution of glucose derivatives, 229
and D. McNicoll, formation of ethers from compounds of the benzoin type, 231
Isoeugenol, oxidation of, 161
Isomerism of ethyl aceto-acetate, 127
Isospartein, conversion of *a*-methylspartein into, 96
"Italian Camphor" (review), 186

JACKSON, C. G., and H. M. Dawson. (*See* Dawson, H. M.)
Jacobsen, J., action of silver nitrate on chloroauric acid and preparation of fulminating gold, 23
Jago, W., lectures on forensic chemistry, 241
James, A. F. B., "Nitrate Facts and Figures" (review), 11
Jerusalem, G., and W. J. Pope, relation between the crystalline form and the chemical constitution of the picryl derivatives, 88
Johnson, C. M., rapid determination of nickel in the presence of chromium, iron, and manganese, 21
Jolibois, P., zinc phosphides, 294
Jones, B. M., spontaneous crystallisation of solutions of some alkali nitrates, 242
E. W. T., simple colorimetric method for the determination of formalin in milk, 247
F., action of selenium and tellurium on arsine and stibine, 13
H. O., and R. W. Everatt. (*See* Everatt, R. W.)
and H. S. Tasker, note on oxalyl chloride, 316
Jorgensen, S. M., "Fundamental Conceptions of Chemistry" (review), 11
Jouve, A., new applications of electro-metallurgical alloys, 15
Jungfleisch, E., and H. Leroux, identity of ilicic alcohol with *a*-amyrine, 305

KANTOROWICZ, H., and F. Sachs. (*See* Sachs, F.)
Kaufler, F., and R. Lorenz. (*See* Lorenz, R.)
Koufmann, L., triphenylstibine sulphide, 222
Keiser, E. H., and L. McMaster, detection of ozone, nitrogen peroxide, and hydrogen peroxide in gas mixtures, 65
"Kelly's Directory of Chemists and Druggists" (review) 45
Kempf, R., and E. Oehler, reaction between ammonium persulphate and sodium peroxide, 197
Kenner, J., and E. Knoevenagel. (*See* Knoevenagel, E.)
Kern, S., high tension bronzes, 273
Ketones, action of mercuric iodide on in alkaline solution, 314
products of reaction of sodamide on, 305
β-alcohol *a a*-dialcoholated, 47
Kiliani, H., products from milk-sugar and calcium hydroxide, 210
King's College, 134
Kipping, F. S., address to the Chemical Section of the British Association, 121
and B. D. W. Luff (*See* Luff, B. D. W.)
Kissling, R., "Das Erdol, seine Verarbeitung und Verwendung" (review) 221
Kjellin electric induction furnace, 29
Knight, Lottie E., and J. K. H. Inglis. (*See* Inglis, J. K. H.)
N., monument to Robert Bunsen, 293
Knoevenagel, E., and J. Kenner, preparation of sulphinic acids, 280
Knoll, R., "Synthetische und Isolierte Reichstoffe und deren Darstellung" (review), 293
Krypton and xenon, densities of, 316

"LABORATORY Arts" (review), 232
"Laboratory Book for the Perfumery Industry" (review). 221
Lactone of dioxy-3 4-butyric acid, 47
Lalin, L., and O. Diels. (*See* Diels, O.)
Landauer, J., "Spectrum Analysis" (review), 58
Lapworth, A., examination of the conception of hydrogen ions in catalysis; salt formation and electrolytic conduction, 317
Law, H. D., and F. M. Perkin, oxidations of hydrocarbons of benzene series, 241
Le Bas, G., new theory of molecular volumes, 85
Le Chatelier, H., precipitated silica, 258
Lea, C., "Kolloides Silber und die Photohaloide" (review), 46
Lead, atomic weight of, 64, 78
in alloys, quantitative estimation, 1
in ores, &c., determination, 105
ethoxide, formation, 34
"Leather Industries Laboratory Book" (review), 131
Leeds, City of, Higher Education Department 148
Institute, Technical School, 148
University, 139
Lees, C. H., resistance of a conductor of uniform thickness whose breadth suddenly changes, 10
Léger, E., aloesol, 294
Lemoine, G., decomposition of alcohols under the catalytic action of live coals, 59
Lenher, V., action of various anhydrous chlorides on tellurium and on tellurium dioxide, 4
homogeneity of tellurium, 27
Leroux, H., and E. Jungfleisch. (*See* Jungfleisch, E.)
Leuchs, H., oxidation of brucine and strychnine, 12
Levy, L. A., fluorescence of platinocyanides, 34
Lewis, S. J., and E. Wedekind. (*See* Wedekind, E.)
"Lewis's Medical and Scientific Circulating Library, Catalogue of" (review), 83
Ley, H., and K. von Engelhardt, ultra-violet fluorescence in cyclic compounds, 233
Leyson, L. T., and G. T. Moody. (*See* Moody, G. T.)
Lime, solubility in water, 244
Liquids, crystalline, transparent clear, 46
fermented, determination of succinic acid in presence of fixed acids in, 245
Lithium in radio-active minerals, 151
Littlebury, W. O., and R. H. Pickard. (*See* Pickard, R. H.)
Liveing, G. D., 8
Liverpool University, 140
Lloyd, F. J., sulphate of ammonia, 172
London, City and Guilds of, Institute, 72, 147
City of, College, 147
East, College, 148, 162
Franco-British Exhibition, 210
University, 133
Lorenz, R., and F. Kaufler, molecular condition of fused salts, 318
Low A. H., technical method for the determination of lead in ores, &c., 105
Luff, B. D. W., and F. S. Kipping organic derivatives of silicon, 266, 278
Luminescence, tribo-, of racemic compounds, 83
Lüppo-Cramer, Dr., "Kolloidchemie und Photographie" (review), 45
"Kolloides Silber und die Photohaloide" (review), 46

MCCAY, L. W., action of hydrogen sulphide on alkaline solutions of zinc salts, 40
McCrae, R. H., isomerism of ethyl aceto-acetate, 127
McDowall, J., mechanism of motion, 61
wave theory of motion, 213
M'Gowan, G., "The Scientific Foundations of Analytical Chemistry" (review), 45
McIlhiney, P. C., method of analysing shellac, 211
M'Intosh, J. G., explosive crystallisation, 59
Mackenzie, J. E., and H. Marshall, trithionates and tetrathionates of the alkali metals, 243
McMaster, L., and E. H. Keiser. (*See* Keiser, E. H.)
McNicoll, D., and J. C. Irvine. (*See* Irvine, J. C.)
Machine, fatigue testing, for metals, 244
Magnesium and alkyl halides, interaction, 232
and monomethylamine, double phosphate of, 47
methyl iodide and amyl ether, crystalline compound of, 44
organic compounds, action on arsenious acid, 222
Malfitano, G., and L. Michel, influence of neutral salts on the hydrolysis of iron perchloride 294
"Malt, Development and Progress of the Manufacture of during the last Forty Years" (review), 10
Manchester Municipal School of Technology, 149
University, 141
Manganese and iron, separation, 105
ferro-magnetic nitrogen compounds of, 318
Margosches, B. M., "Die Chemische Analyse" (review), 196
Marples, M. E., and A. W. Titherley. (*See* Titherley, A. W.)
Marsden, Effie G., and E. C. C. Baly. (*See* Baly, E. C. C.)
Marsh, J. E., and R. de J. F. Struthers. (*See* Struthers, R. de J. F.)
Marshall, H., and J. E. Mackenzie. (*See* Mackenzie, J. E.)
Martindale, W. H., and W. W. Westcott, "Extra Pharmacopœia" (review), 257
"Matriculation Directory" (review), 94
Matter, indestructibility of, 178
Mauguin, C., action of bromine on ether 250
Maurichéau-Beaupré, M., new method of making pure hydrogen, 173
Mayer, M., and V. Almayer, methane syntheses with calcium hydride, 234
reactions between nickel and hydrogen, 234
Mech, M., products of condensation of *o*- and *p*-nitrated benzile with acetylacetone, 60
Meldola, R., and J. G. Hay, molecular compound of trinitroacetylaminophenol and *β*-naphthol 255
syntheses with phenol derivatives containing a mobile nitro-group, 242
Meldrum, A. N., and W. H. Perkin, jun., cis- and trans-modifications of 1-methylcyclohexan-2-*ol*-4-carboxylic acid and their conversion into 1-methyl-Δ^1-cyclo-hexene-4-carboxylic acid, 230
Melzer, W., silicon acids and their derivatives, 281
Menthols, isomeric, 257
Merck, E., "Chemical Reagents" (review), 22
Mercury cyanide, compounds with alkalis and with nitric acid, 12
zirconium, double salt, 234
Messinger and Vortmann's method of estimating phenols, 60
"Metal, &c., Decoration of" (review), 23
Metals, demonstration in the rapid electro-analytical separation of, 163
fatigue testing machine for, 244
of aluminium group and organic halogen derivatives, interaction, 241
rapid electro analytical deposition and separation of, 230

Methane, syntheses with calcium hydride, 234
synthesis of, 265
Methyl derivatives of pyridine, chlorination, 266
Methylation in ethylene derivatives, 174
Methyl ethers of catechol derivatives, action of phosphorus pentachloride on, 278
2-Methylpyridine, 266
Methylspartein, *a*-, conversion into isospartein, 96
cyclisation of, 305
Metzger, F. J., and H. T. Beans, electrolytic determination of bismuth, 202
Michel, L., and G. Malfitano. (*See* Malfitano, G.)
Micklethwait, Frances M. G., and G. T. Morgan. (*See* Morgan, G. T.)
Micro balance, use for determination of electro-chemical equivalents and for measurement of densities of solids, 229
Milk, determination of formalin in, 247
lectures on, 205
sugar and calcium hydroxide, products from, 210
Miller, Ivy, and R. B. Moore. (*See* Moore, R. B.)
Mills, W. H., and S. T. Widdows, benzeneazo-2-pyridone, 33
"Minerals, Pocket Handbook of" (review), 58
Minerals, decomposition by means of sodium peroxide and metallic sulphides, 61, 76
influence of fine grinding on the water and ferrous-iron content of, 205, 215
radio-active, lithium in, 151
Molecular volumes, new theory of, 85
weights of phosphoric acids determined by cryoscopy, 60
Molybdenum, new element allied to, 261
Momber, W., "Der Dampf in der Chemischen Technik" (review), 196
Mono, L., H. Hirtz, and M. D. Cowap, note on a volatile compound of cobalt with carbon monoxide, 165
Monobromaldehyde, 280
Monochloromethyl ether, action on sodium derivatives of ethyl malonate and ethyl isopropylmalonate, 255
Monomethylamine and magnesium, double phosphate of, 47
preparing, 170, 258
Moody, G. T., and L. T. Leyson, solubility of lime in water, 244
Moore, R. B., densities of krypton and xenon, 316
and Ivy Miller, separation of iron from manganese, 105
Morgan, G. T., and Frances M. G. Micklethwait, organic derivatives of arsenic, 315
Morrow, J., lateral vibration and deflection of clamped-directed bars, 9
Motion, mechanism of, 61
wave theory of, 213, 232
Moulton, H. F., and J. Roberts. (*See* Roberts, J.)
Muntz, A., and P. Nottin, agricultural use of calcium cyanamide, 318

NAPHTHALENE series, migration of naphthyl group in iodohydrins of, 258
Naphthol, *β*-, and trinitroacetyl aminophenol, molecular compound of, 255
Naphthyl group, migration in iodohydrins of the naphthalene series, 258
Neo-erbium oxide, spectrum, 318
Neumann, B., "Post's Chemisch-Technische Analyse" (review), 23, 232
Newcastle-on-Tyne, Armstrong College, 140
Nicholson, J. W., inductance of two parallel wires, 10
Nickel, action of arsenic trichloride on, 166
and cobalt, detection when present together, 24
and hydrogen, relations between, 234
in steel, determination, 38
steel, gases occluded in, 162
Nicolardot, P., new method of opening up ferro-alloys, 258
separation of tungstic acid and silica, 294
"Nitrate Facts and Figures" (review), 11
Nitrate, mercuric, solution, solubility of silver chloride in, 22
mercurous, as a micro-chemical reagent for arsenic, 280
Nitroamines, aromatic, and allied substances, transformation and relation to substitution in benzene derivatives, 164
Nitroaminobenzenes, transformation into nitroanilines, 164
Nitroaminobromobenzenes, wandering of bromine in transformation of, 165
Nitroanilines, transformation of nitroaminobenzenes into, 164
Nitrobenzyl disulphides, 229
Nitro-compounds, reduction with zinc dust and acetic acid, 222
Nitrogen, atomic weight, 318
compounds, effect of constitution on the rotatory power of optically active, 255
thermo-chemical equivalence and the thermo-chemistry of, 226
cycles, synthesis of, 60, 96
atmospheric, production of ammonia from by means of peat, 163
peroxide in gas mixtures, detection, 65
Nitroso- and nitro-groups, 22
Northampton Polytechnic Institute, 148
Northern Polytechnic Institute, 148
Nottin, P., and A. Muntz. (*See* Muntz, A.)
Nottingham, University College, 142
Noyes, W. A., chemical publications in America in relation to chemical industry, 75
A. A., W. C. Bray, and E. B. Spear, system of qualitative analysis for the common elements, 6, 16, 32, 41, 55, 71 81, 92, 107, 160, 171, 181, 194, 208, 219, 228, 239, 251, 264, 273, 291, 300, 311
Nucleoprotein, reaction distinguishing phosphoprotein from, 243
Nutmeg oil, constituents of expressed, 242

OBITUARY, John Trevor Cart, 196
Oehler, E., and R. Kempf. (*See* Kempf, R.)
Ogawa, M., preliminary note on a new element allied to molybdenum, 261
on a new element in thorianite, 249
Oil of nutmeg, constituents of expressed, 242
Olefines, ozonides of simple, 246
Onnes, K., liquefaction of helium, 37
Optical activity and unsaturation, relation between, 229, 241
Ores, &c., determination of lead in, 105
Ortho-di-amino compounds, preparation, 47
a-Osazones, stereoisomeric, alternative structure for, 33
Ostwald, W., "Kurzes Lehrbuch der Organischen Chemie" (review), 250
"The Scientific Foundations of Analytical Chemistry" (review), 45
Oxalyl chloride, 282, 316
Oxford University, 133
Oxidation of brucine and strychnine, 12
of isoeugenol, 161
of phosphorous acid by iodine, 231
products of sitosterol, 267
Oxidations of hydrocarbons of benzene series, 241
Oxides of sulphuretted hydrogen, 281
reduction of refractory by carbon, 230
metallic, action on primary alcohols, 59, 83, 96
Oxydasic phenomena produced by colloidal iron ferrocyanide, 280
Oxygen, carbon, and hydrogen, thermo-chemical relations of, 46, 82
Ozokerite, 210
Ozone in gas mixtures, detection, 65
thermal decompositions of, 230
Ozonides of simple olefines, 246

PAAL, C., and J. Gerum, catalytic reductions with colloidal palladium and platinum, 186
and K. Roth, catalytic reductions with colloidal palladium, 186
Paine, H. H., and W. C. D. Whetham. (*See* Whetham, W. C. D.)
"Painting, House" (review), 258
Palladium, colloidal, catalytic reductions with, 186
septum, passage of hydrogen through, 254
Palmer, H. E., and P. E. Browning. (*See* Browning, P. E.)
Pantogen, atomic weight of, 294
"Paper Makers' Directory of all Nations" (review), 131
Paraffin, 210
Para-nitroaniline, chlorination of, 255
Para-nitrotoluene, action of caustic alkalis on, 243
Paratoluidine, action of ethyl pyruvate on, 96
Paris, L., fused amorphous alumina and production of artificial sapphires, 318
Parry, L., "Analysis of Ashes and Alloys" (review), 196
Pascal, P., relation between the magnetic and chemical properties of complex salts containing iron, 83
"Patents and Designs Act, 1907" (review) 10
Patents and designs, 96
compulsory working of, 161
Patterson, T. S., influence of solvents on the rotation of optically active compounds, 257
Pearson, C., wandering of bromine in the transformation of nitroaminobromobenzenes 165
Pélabon, H., tellurides of arsenic and bismuth, 60
Pelet-Jolivet, L., and A. Wild, state of colouring matters in solution, 258
"Perfumery industry, Laboratory Book for" (review), 221
"Perfumes, Synthetic and Isolated, and their Preparation" (review), 293
Perhalogen salts, 231
Perkin, F. M., note on formation of lead ethoxide, 34
and Mary Cunningham. (*See* Cunningham, M.)
Perkin, F. M., and H. D. Law. (*See* Law, H. D.)
W. H., jun., and K. Fisher. (*See* Fisher, K.)
V. J. Harding, and W. N. Haworth. (*See* Harding, V. J.)
and A. N. Meldrum. (*See* Meldrum, A. N.)
Perman, E. P., direct action of radium on copper and gold, 256
Perseulose, 117
Peters, W., zirconium-mercury double salt, 234
"Petroleum, its preparation and Applications" (review), 221
Pharmaceutical Society, School of Pharmacy of, 136
"Pharmacopœia, Extra" (review), 257
Phenols, action of iodine on, 316
estimating, Messinger and Vortmann's method, 60
Phenylhydrazine, reactions with metallic cyanides and other salts, 34
S-Phenylphenazothionium, derivatives of, 243
Phillips, H. E. W., electrical conductivity of phosphoric acid, 279
Phosphate of magnesium and monomethylamine, double, 47
Phosphoprotein, reaction distinguishing from nucleoprotein, 243
Phosphorescence, ionisation by phosphorus and, 305
Phosphorus, action of ammonia on, 11
and phosphorescence, ionisation by, 305
atomic volumes of, 256
pentachloride, action on methylene ethers of catechol derivatives, 278
Photographic plates, electric splashes on, 269
"Photography, Colloidal Chemistry and" (review), 45
"Photo-haloids, Colloid Silver and" (review), 46
Phthaleins of mellitic and pyromellitic acids, constitution of, 254
salts of, constitution of, 253
Physical Society 8, 193, 244, 265, 303
Exhibition, 282
Physiological action and chemical constitution, relation between in substituted amino-alkyl esters, 254
Pickard, R. H., and W. O. Littlebury, isomeric menthols, 257
and J. Yates, contributions to the chemistry of the cholesterol group, 242, 267
Picrates, 24, 232
Picryl derivatives, relation between crystalline form and chemical constitution, 88
Pilcher, R. B., appointment of Public Analyst for the Metropolitan Borough of Shoreditch, 161
Pintza, A., and P. A. Guye. (*See* Guye, P. A.)
"Plants, Chemistry and Biology of the Secretions of" (review), 120
Platinocyanides, fluorescence of, 34
Platinum, colloidal, catalytic reductions with, 186
in so-called pure borax, 210
metals in chemicals used for assaying, 104
Plimmer, R. H. A., proteins of egg-yolk, 231
and F. H. Scott, reaction distinguishing phosphoprotein from nucleoprotein, and the distribution of phosphoproteins in tissues, 243
Polarisation, elliptic, 304

Pollard, W. B., rapid method of qualitative analysis, 211
Poly-carbon groups, relative stability of cyclic, 221
Polyiodides, formation in nitrobenzene solution, 35, 256
Polymorphism, 231
Polyphenols, hydrogenation, 23
Polytechnic, 148
Pope, F. G., and R. Fleming, colour and constitution of azomethine compounds, 267
W. J., and W. Barlow. (*See* Barlow, W.)
and G. Jerusalem. (*See* Jerusalem, G.)
Porter, A. W., electric splashes on photographic plates, 269
Poschl, V., "Einfuhrung in die Kolloidchemie" (review), 293
"Post's Chemisch - technische Analyse" (review), 23, 232
Potash bulb, new form of, 38
Potassium hydroxide, action of fused on cholesterol, 242
iodide, double salts of with mercuric iodide and dimercuriodocamphor in organic solvents, 314
sodium alloy, photo-electric properties of, 268
sulphates, acid, 96
Poulenc, C., "Les Nouveautés Chimiques pour 1908" (review), 23
Power, F. B., and A. H. Salway, constituents of the expressed oil of nutmeg, 242
Pozzi-Escot, E., determination of succinic acid in presence of fixed acids in wines and fermented liquids, 245
new method of determining the fixed and volatile acids in wines, 162
Price, T. S., and D. F. Twiss, preparation of disulphides, 34, 229, 242
Prideaux, E. B. R., atomic volumes of phosphorus, 256
Pring, J. N., formation of some carbides, 279
Pritze, M., and A. Rosenheim. (*See* Rosenheim, A.)
Procter, H. R., colloidal chemistry, 152, 167, 175
"Leather Industries Laboratory Book" (review), 131
Proteins of egg-yolk, 231
Public appointments, tendering for, 197
Pyman, F. L., relation between chemical constitution and physiological action in certain substituted aminoalkyl esters, 254
M. Barrowcliff, and F. G. P. Remfry. (*See* Barrowcliff, M.)
and W. C. Reynolds, meteloidine, 277
Pyridine, chlorination of methyl derivatives of, 266
chlorine derivatives of, 266, 267
4-Pyrone compounds, formation from acetylenic acids, 34
Pyrones and allied compounds 315

RACEMIC compounds in liquid state, 256
triboluminescence of, 83
Radio-active changes in the earth, 73
minerals, lithium in, 151
Radio-activity, present state of our knowledge of, 235, 247, 259, 271, 289, 300
Radium, action on copper and gold, 256
emanation, action on solutions of copper salts, 157
formation of mists in presence of, 156
present in some "tufa" deposits from Hot Springs, Arkansas, 199
rate of production of helium from, 188
Ramsay, A. A., formation of formaldehyde in solutions of canesugar, 288
Rankin, D. J., potential energy of the elements, 23, 59, 120, 174
Rankine, A. O., rate of growth of viscosity in congealing solutions, 269
Ray, P. C., molecular volumes of the nitrites of barium, strontium, and calcium, 279
Reaction between ammonium persulphate and sodium peroxide, 197
between silver sulphide and silver sulphate, 281
distinguishing phospho-protein from nucleo-protein, 243
of bromine on benzaldehyde, velocity of, 198
of sodamide on ketones, 305
Reactions, colour, produced by sodium hypobromite, 200
of dichloro-urea, 166
of phenylhydrazine, 34
microchemical, of arsenic applicable in forensic chemistry, 245
"Reagents, Chemical" (review), 22
Recoura, A., colloidal barium sulphate, 46
Redgrove, H. S., calculation of thermal constants of aromatic substances, 80
constitution of the carbon molecule, 72
potential energy of the elements, 11, 46
thermo-chemical evidence for von Baeyer's strain theory, 25
wave theory of motion, 232
Redruth School of Mines, 148
Reductions, catalytic, with colloidal palladium and platinum, 186
Reed, W. W., transformation of nitroaminobenzenes into nitroanilines, 164
Reeks, Margaret, "Hints for Crystal Drawing" (review), 293
Refracting surfaces, graphic method of dealing with, 303
Reischle, F. and R. F. Weinland. (*See* Weinland, R. F.)
Remfry, F. G. P., M. Barrowcliff and F. L. Pyman. (*See* Barrowcliff, M.)
"Report, Annual, on the Progress of Fabric Printing and Allied Industries" (review), 197
Reynolds, W. C., and F. L. Pyman. (*See* Pyman, F. L.)
Rhodamines of mellitic acid, 253
Rhodanides of inorganic radicles, constitution and properties of, 279
Rich, Elizabeth M., isomeric chromous chlorides, 256
Richmond, H. D., women and the Chemical Society, 58
Riesenfeld, E. H., chromium tetroxide compounds, 282
decomposition of chromic acid by hydrogen peroxide, 233
Rimele, E., and T. Curtius. (*See* Curtius, T.)
Ringe, O., and F. Fischer. (*See* Fischer, F.)
Roberts, J., and H. F. Moulton, "Patents and Designs Act, 1907" (review), 10
Rochling - Rodenhauser electric induction furnace, 29
Rocks, influence of fine grinding on the water and ferrous-iron content of, 205, 215
Rose, J. G., existence of platinum metals in chemicals used for assaying, 104
Rosenheim, A., and M. Pritze, molecular weight and hydrate of hypophosphoric acid, 222
Rosset and Besson, MM. (*See* Besson, M.)
Rotarski, T., liquid crystals, 47
Roth, K., and C. Paal. (*See* Paal, C.)
Roy, C. S., and O Silberrad. (*See* Silberrad, O.)
Royal College of Science and Royal School of Mines, 282
Institution, 36, 225, 232, 258, 292, 294
Society, 282
of Arts, 12 270
Rubber, strength or nerve of crude, 317
Ruff, O., silicon iodoform, 318
and F. Eisner, titanium nitride and a new class of titanium compounds, 186
and J. Zedner, solutions of alkali metals in liquid ammonia, 24
Ruhemann, S., formation of 4-pyrone compounds from acetylenic acids, 34
Rule, A., action of nitrous gases on dicyclopentadiene, 33
Russ, S., diffusion of actinium and thorium emanations, 304

SABATIER, P., and A. Mailhe, action of metallic oxides on primary alcohols, 59, 83, 96
direct hydrogenation of polyphenols, 23
Sabin, A. H., "House Painting" (review), 258
Sachs, F., and H. Kantorowicz, action of magnesium organic compounds on arsenious acid, 222
Sackur, O., reaction between silver sulphide and silver sulphate, 281
St. Andrew's University, 143, 145
Sakurai, Prof., jubilee of, 249
Salicylaldehyde, condensation of, 268
Salt, zirconium-mercury double, 234
Salts influence of neutral on the hydrolysis of iron perchloride, 294
of acetato-chromium base, 234
of organic acids, electrolytic chlorination, 33
of phthaleins, constitution, 253
complex, containing iron, relation between magnetic and chemical properties of, 83
fused, molecular condition of, 318
iodopentamminocobaltic, 233
thiosulphonic acid, action of arsenite and cyanide on, 231
Salway, A. H., and F. B. Power (*See* Power, F. B.)
"San Francisco Earthquake and Fire of April 18, 1906" (review), 45
Sand, H. J. S., demonstration in the rapid electro-analytical separation of metals, 163
rapid electro-analytical deposition and separation of metals, 230
Sansone, A., "Jahresbericht Uber die Fortschritte des Zeugdrucks und Verwandter Industrien" (review), 197
Sapphires, production of artificial, 318
Scandium, 274, 283, 295, 307
Schaefer, K., and E. C. C. Baly. (*See* Baly, E. C. C.)
Scheiber, J., constitution of copper acetylide, 318
Schenck, H., "Chemical Reagents" (review), 22
R., and V. Falcke, hydrogen persulphide, 198
Schidrowitz, P., structure of crude indiarubber, 317
and H. A. Goldsbrough, viscosity of indiarubber and indiarubber solutions, 317
Schlundt, H., electroscopic determination of the radium present in some tufa deposits from Hot Springs, Arkansas, 199
Schmachtenberg, H., and C. Bulow. (*See* Bulow, C.)
Schmidlin, J., coloured and colourless triphenylmethyl, 186
Scholz, H. A., and J. H. Walton, jun. (*See* Walton, J. H., jun.)
Scholtz, M., stereoisomerism in compounds with asymmetric carbon and pentavalent asymmetric nitrogen, 48
Schorigin, P., new synthesis of aromatic carboxylic acids from hydrocarbons, 222
Scott, F. H., and R. H. A. Plimmer. (*See* Plimmer, R. H. A.)
S. F., and W. M. Dehn. (*See* Dehn, W. M.)
Selenium, action on arsine and stibine, 13
Senderens, J. B., catalytic dehydration of organic compounds, 23
Senier, A., 241
Sewell, J. S., "The San Francisco Earthquake and Fire of April 18, 1906" (review), 45
Sheffield University, 142
Shellac, analysiog, 211
Shoreditch, appointment of Public Analyst for the Metropolitan Borough of, 161
Shukoff, I., magnetic oxides of chromium, 78
Shutt, F. T., "Alkali Soils, their Nature and Reclamation" (review), 11
Silberrad, O., constitution of the phthaleins of mellitic and pyromellitic acids, 254
and C. S. Roy, relationship of colour and fluorescence to constitution, 253
Silica and tungstic acid, separation, 294
anhydride, separating, 47
precipitated, 258
Silicon and silver alloys, 305
organic derivatives of, 266, 278
acids and their derivatives, 281
iodoform, 318
"Silver, Colloid, and the Photohaloids" (review), 46
Silver and silicon alloys, 305
atomic weight of, 305
chloride, solubility in mercuric nitrate solution, 22
iodide in ammonia, solubility of, 46
nitrate, action on chloroauric acid, 23
sulphate and silver sulphide, reaction between, 281
Simon, L. J., mechanism of synthesis of nitrogen cycles, 60, 96
Simon, O., "Laboratoriumsbuch für die Industrie der Riechstoffe" (review), 211
Simonsen, J. L., syntheses with the aid of monochloromethyl ether, 255
Sir John Cass Technical Institute, 148
Sitosterol, oxidation products of, 267
Slator, A., factors which influence the rate of alcoholic fermentation, 175
Smiles, S., and Maud Gazdar. (*See* Gazdar, M.)
and T. P. Hilditch, derivatives of S-phenylphenazothionium, 243
Smith, A., "General Inorganic Chemistry" (review), 186
Society of Chemical Industry, 257, 317
of Public Analysts, tendering for Public Appointments, 197
Soda, caustic, solution, action of cold on cellulose, 234
Sodamide, products of reaction on ketones, 305
Sodium compound of fluorene, 233
alkyl thiosulphates, action of alkalis on, 34

Sodium benzylate, condensation with propyl, butyl, and isoamyl alcohols, 60
hydroxide, solution for making standard solutions of, 108
hypobromite, colour reactions produced by, 200
nitrate, consumption of, 83
peroxide and ammonium persulphate, reaction between, 197
comparative oxidising power of, 206
decomposition of minerals and industrial products by, 61, 76
Solids, use of micro-chemical balance for measurement of densities of, 229
Solution for making standard solutions of sodium hydroxide, 108
Solutions, processes operative in, 1
aqueous, viscosity and conductivities of, 230
Solvents, influence on rotation of optically active compounds, 257
Soper, G. A., "Air and Ventilation of Subways" (review), 280
Soulé, F., "San Francisco Earthquake and Fire of April 18, 1906" (review), 45
Spark, short, phenomena, 225
Sparteine, 96
Spear, W. B., A. A. Noyes, and W. C. Bray. (*See* Noyes, A. A.)
Spectra, absorption, and chemical constitution, relation between 22, 254, 266, 278, 315
"Spectrum Analysis" (review), 58
Spencer, J. F., lecture experiments to prepare hydrocarbons, 186
and Mary S. Crewdson, direct interaction of magnesium and alkyl halides, 232
and Marion L. Wallace, interaction of the metals of the aluminium group and organic halogen derivatives, 241
Staffordshire Society, 159
Standage, H. C., "Decoration of Metal, Wood, Glass, &c." (review), 23
Stanton, Dr., fatigue testing machine for metals, 244
Staudinger, H., oxalyl chloride, 282
"Steam in Technical Chemistry" (review), 196
Steel, determination of nickel and chromium in, 38
Steele, B. D., oxidation of phosphorous acid by iodine, 231
Stereoisomerism in compounds with asymmetric carbon and pentavalent asymmetric nitrogen, 48
Stibine, action of selenium and tellurium on, 13
Stilbene group, colouring matters of, 243
Stock, A., action of ammonia upon phosphorus, 11
and W. Holle, preparation of boron nitride and of calcium boride, 48
Stockton, Edith, and C. G. Eldredge, fruit of the Caulophyllum thalictroides and Cornus sericea, 190
Strachan, J., notes on a new primary voltaic cell of the Daniell type, 102
Strain theory, thermo-chemical evidence for von Baeyer's, 25
Strontium and barium oxides, hydrates of, 120
nitrites, molecular volumes of, 279
Strutt, R. J., radio-active changes in the earth, 73
Strychnine oxidation, 12
Stubbs, A. J., and A. E. Dunstan. (*See* Dunstan, A. E.)
Substances, hydro-aromatic, study of, 226, 236
"Subways, Air and Ventilation of" (review), 280
Sugar, cane, formation of formaldehyde in solutions of, 288
crystallised, 117
Suida, W., picrates, 24
Sulphides and hydrogen dioxide, interaction, 256
metallic, decomposition of minerals and industrial products by, 61, 76
dl-Sulphobenzylethylisobutyl-silicyl oxide, synthesis of, 266
Sulphoxides, preparation and constitution, 233
Sunlight, effects upon colourless glass, 100
Syntheses, methane, with calcium hydride, 234
with aid of monochloro methyl ether, 255
with phenol derivatives containing a mobile nitro-group, 242
Synthesis of apocynin, 21
of aromatic carboxylic acids from hydrocarbons, 222
of complex acridines, 243
of iodoacetic-nitrile, 48
of methane, 265
of 1-methylcyclohexylidene-4-acetic acid, 268
of nitrogen cycles, 60, 96
of *dl*-sulphobenzylethylisobutylsilicyl oxide, 266
of terpenes, 267
of thionaphthen derivatives from styrenes and thionyl chloride, 278
Szilard, B., "Beiträge zur Allgemeinen Kolloidchemie" (review), 46

TANRET, C., ergosterin and tungisterin, 79
Tasker, H. S., and H. O. Jones. (*See* Jones, H. O.)
Tautomerism, enol-ketonic, 266
Taylor, J., and A. E. Dixon, (*See* Dixon, A. E.)
Teichmann, H., "Komprimierte und Verflussigte Gase" (review), 270
Telegraphy, wireless, experiments on a directive system of, 8
Telluride ores, assay of, 180
Tellurium, cryoscopic constant of, 60
dicyanide, 315
Tenoering for public appointments, 197
Terpenes, synthesis of, 267
Tetramethyldiaminobenzhydryl methylene compounds, constitution, 47
Thallium analysis, 6, 16, 32, 41, 55, 71, 81, 92, 107, 160, 171, 181, 194, 208, 219, 228, 239, 251, 264, 273, 291, 301, 311
"Therapeutics, Report of Recent Advances in Pharmaceutical Chemistry and" (review), 270
Thermo-chemical equivalence and the thermo-chemistry of nitrogen, 226
Thermo regulator, form of, 49
Thiele, J., preparation of hydrazoic acid, 222
Thionaphthen derivatives from styrenes and thionyl chloride, synthesis of, 278
Thole, F. B. T., and A. E. Dunstan. (*See* Dunstan, A. E.)
Thomlinson, J. C., constitution of the carbon molecule, 37
thermo-chemical relations of carbon, hydrogen, and oxygen, 46, 83
equivalence and the thermo-chemistry of nitrogen, 226
thermochemistry of aluminium, 197
Thorianite, new element in, 249
Thorium and actinium emanations, diffusion of, 304
Thorpe, J. F., and N. A. Creeth. (*See* Creeth, N. A.)
Tibbles, W., "Theory of Ions" (review), 94
Tiffeneau, M., and Daudel, M., migration of naphthyl group in iodohydrins of the naphthalene series, 258
Tilden, W. A., rusting of iron, 20
Tin and antimony, separation, 230
Tingle, J. B., "Spectrum Analysis" (review), 58
Tinkler, C. K., studies of the perhalogen salts, 231
Titanium analysis, 6, 16, 32, 41, 55, 71, 81, 92, 107, 160, 171, 181, 194, 208, 219, 228, 239, 251, 264, 273, 291, 300, 311
compounds, new class of, 186
iodide, 83
nitride, and a new class of titanium compounds, 186
Titherley, A. W., and M. E. Marples, condensation of salicylaldehyde and benzamide, 268
Tollens, B., simple test for glycuronic acid by means of naphthoresorcin, hydrochloric acid, and ether, 24
Tosi, A., and E. Bellini. (*See* Bellini, E.)
Triazoacetaldehyde, 267
Triazoethylalcohol, 267
Triazo-group, 267
2 : 3 : 5-Trichloropyridine, orientation, 267
Trinitroacetylaminophenol and β-naphthol, molecular compound of, 255
Triphenylmethane series, cause of colour in, 253
Triphenylmethyl, coloured and colourless, 186
Triphenylstibine sulphide, 222
Tsakalotos, D., passage of hydrogen through a palladium septum and the pressure which it produces, 254
Tschirch, A., "Chemie und Biologie der Pflanzlichen" (review), 120
Tuck, W. B., and E. C. C. Baly. (*See* Baly, E. C. C.)
Tufa deposits from Hot Springs, Arkansas, electroscopic determination of radium present in, 199
Twiss, D. F., and T. S. Price. (*See* Price, T. S.)

UNIVERSITY College, 134
Tutorial College, 148
Unsaturation and optical activity, relation between, 229, 241
Uranium analysis, 6, 16, 32, 41, 55, 71, 81, 92, 107, 160, 171, 181, 194, 208, 219, 228, 239, 251, 264, 273, 291, 300, 311
"Urbanora, the World's Educator" (review), 45
Urea, action of chlorine on, 285

VALEUR, A., new method of cyclisation of *a*-methyl spartein, 305
spartein, 96
Vanadium analysis, 6, 16, 32, 41, 55, 71, 81, 92, 107, 160, 171, 181, 194, 208, 219, 228, 239, 251, 264, 273, 291, 300, 311
and iron, estimation in presence of one another, 80
Veit, T., and E. Wedekind. (*See* Wedekind, E.)
Veley, V. H., affinity constants of bases as determined by the aid of methyl-orange, 278
of certain alkaloids for hydrochloric acid, 277
"Ventilation and Air of Subways" (review), 280
Veses, M., preparation of alkaline chloroiridites, 60
Vicianine, constitution of, 162
Viewig, W., action of cold caustic soda solution on cellulose, 234
Vignon, L., and M. Evieux, heat of neutralisation of acetic acid and benzoic acid by aniline in a benzene medium, 47
heat of neutralisation of picric acid by different aromatic bases in benzene, 83
Vigouroux, E., action of arsenic trichloride on nickel and on arseno-nickels, 166
Viscosity and chemical constitution, relation between, 256, 266
of indiarubber and indiarubber solutions, 317
rate of growth of in congealing solutions, 269
Von Baeyer's strain theory, thermo-chemical evidence for, 25
Von Braun, J., characterisation of primary, secondary, and tertiary bases with 1 . 5-dibrompentane, 48
double dissociation of quaternary ammonium compounds and synthesis of iodoaceto-nitrile, 48
Von Engelhardt, K., and H. Ley. (*See* Ley, H.)
Von Liebig, H., preparation of benzilic acid, 12
Von Welsbach, C. A., decomposition of ytterbium into its elements, 223, 297
Vorlander, D., transparent clear crystalline liquids, 46
Vortmann and Messinger's method of estimating phenols, 60

WAGNER, H., and K. A. Hofmann. (*See* Hofmann, K. A.)
Wahl, A., preparation of benzoylacetic ethers, 84
Wales, University College of 136
North, University College of, 136
South, geological survey on the coals of, 12
University College of, 137
Walker, J., elliptic polarisation, 304
Wallace, Marion L., and J. F. Spencer. (*See* Spencer, J. F.)
Walton, J. H., jun., and H. A. Scholz, decomposition of certain minerals and industrial products by means of sodium peroxide and metallic sulphides, 61, 76
Warren, C. M., and W. Elborne. (*See* Elborne, W.)
Watson, H. E., E. C. C. Baly, and J. N. Collie. (*See* Baly, E. C. C.)
Waxes, cerasin, 210
Wedekind, E., and S. J. Lewis, studies on zirconium, 21
and T. Veit, ferromagnetic nitrogen compounds of manganese, 318
Weed, L. H., and F. A. Gooch. (*See* Gooch, F. A.)
Weinland, R. F., salts of an acetato-chromium base, 234
Weinland, R. F., and F. Reischle, hydrofluorides of weak organic bases, 318
Weissgerber, R., sodium compound of fluorene, 233
Weisweiller, G., and G. Bertrand. (*See* Bertrand, G.)
Werner, A., formic and acetic acid salts of chromium, 282
iodopentamminocobaltic salts, 233
Westcott, W. W., and W. H. Martindale. (*See* Martindale, W. H.)

Weston, F. E., explosive crystallisation, 27
Whetham, W. C. D., and H. H. Paine, electrolytic properties of dilute solutions of sulphuric acid, 98, 118, 127, 158
Wharton, C. C., dyes soluble in petrol, 162
Widdows, Sibyl T., and W. H. Mills. (*See* Mills, W. H.)
Wiesbaden Chemical Laboratory, 149
Wild, A., and L. Pelet-Jolivet. (*See* Pelet-Jolivet, L.)
Williams, Katharine A., official methods of American agricultural chemists, 198
Wilson, J. H., and G. P. Baxter. *See* Baxter, G. P.)
Wilson, R. W., and A. E. Dunstan. (*See* Dunstan, A. E.
Wines, analysis of, 56, 174
determination of succinic acid in presence of fixed acids in 245
determining the fixed and volatile acids in, 162
Wires, inductance of two parallel, 110
Wolff, J., oxydasic phenomena produced by colloidal iron ferrocyanide, 280
Woltereck, H. C., dissociation temperature of ammonia and carbon monoxide, 197
production of ammonia from atmospheric nitrogen, by means of peat, 163
Wolverhampton Municipal Science and Technical School, 149
Women, proposal to admit to Chemical Society, 17, 35, 58, 94, 173, 245, 252
"Wood, &c., Decoration of" (review), 23
Woods, G. J., chrome alum, 305
Woollatt, G. H., "Laboratory Arts" (review), 232
Wootton, F., and J. K. H. Inglis. (*See* Inglis, J. K. H.)
"Works' Chemist" (review), 196

XENON and krypton, densities of, 316

YATES, J., and R. H. Pickard. (*See* Pickard, R. H.)
Ytterbium, decomposition into its elements, 223, 297

ZEDNER, J., and O. Ruff. (*See* Ruff, O.)
Zerewitinoff, T., crystalline compound of magnesium methyl iodide with amyl ether, 44
Zinc phosphides, 294
salts, action of hydrogen sulphide on alkaline solutions of, 40
Zirconium analysis, 6, 16, 32, 41, 55, 71, 81, 92, 107, 160, 171, 181, 194, 208, 219, 228, 239, 251, 264, 273, 291, 300, 311
studies on, 21
mercury double salt, 234

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